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Comparison of Monitoring Approaches for Selected Priority Pollutants in Surface Water CMA on-site 2

A Chemical Monitoring Activity Initiative in support to the Water Framework Directive implementation

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1 Abstract

27 Analytical Laboratories from eleven EU Member States and two non-EU countries have participated in a technical on-site event during which sampling and analytical methodologies for chemical monitoring according to proposed WFD provisions have been compared. Coordination of the project was provided by the European Commission Joint Research Centre in collaboration with the Italian Water Research Institute, the Hungarian Ministry of Environment and Water and the Serbian Ministry for Environment and Spatial Planning. The Laboratories had been invited to take samples from a major European river according to their standard protocols and to analyse them for PAHs, PBDE and Nonyl-, Octylphenol.

It was shown that even some of the most challenging WFD priority substances, selected on purpose for this exercise, can be measured at WFD relevant concentrations (0.3 x EQS) with methods currently applied in Member States. Depending on the analyte group, the obtained results were not within proposed data quality limits for some participants and therefore further development of methods and harmonisations of efforts is suggested.

2 Introduction

2.1 EU legislation for control of chemical pollutants

The Water Framework Directive (WFD) (2000/60/EC) shall provide regulation for the contamination of European water bodies through chemical pollutants. This is achieved via the Priority Substance List Decision (2455/2001/EC) and establishing of Environmental Quality Standards on European level through the Daughter Directive 2008/105/EC. For river basin specific pollutants the Water Framework Directive provisions include obligations for identification of relevant pollutants at smaller spatial scales and the derivation of appropriate limit values on national level. The Groundwater Directive (2006/118/EC) ensures the protection of groundwater against pollution and deterioration. Therefore, Member States should set-up water monitoring programs covering a wide range of possible contaminants in order to identify risks, priority issues and needs for action.

While at time of the CMA on-site 2 event, mid September 2008, the proposed text COM(2006)398 had been available, the EQS Directive 2008/105/EC has been approved by European Parliament and European Council only in December 2008. There have been no changes in the limit values proposed at time of the event and the limit values in the approved Directive.

2.2 WFD Environmental Quality Standards Directive

The WFD daughter Directive 2008/105/EC on Environmental Quality Standards in the Field of Water Policy is regulating the pollution with chemical substances in European waters. The performance criteria are proposed in a draft Commission Directive on Analytical Quality Control.

JRC IES has been accompanying the preparation of the upcoming WFD Daughter Directive COM(2006)398 on Environmental Quality Standards EQS through chairing the workgroup on Analysis and Monitoring of Priority Substances AMPS (2003-2004), co-chairing the drafting of the CMA guidance document for surface waters within the Chemical Monitoring Activity CMA (2005-2006) and is currently co-chairing the Chemical Monitoring Activity in 2007-2009. The assessment of available methods for WFD compliance checking is among the prime objectives of the chemical monitoring activity. It is important that methodologies fulfil the requirements of the WFD chemical monitoring, e.g. by delivering concentration data of sufficient quality in order to assess compliance with the WFD Directive. Guidance on general WFD monitoring provision is available through the Guidance Document No. 7 “Monitoring under the Water Framework Directive” and for implementation of the ground water through the WFD CIS Guidance Document No. 15 “Guidance on Groundwater Monitoring” and CIS guidance document No 19 on “Chemical Monitoring of Surface Waters”.

2.3 Chemical Monitoring Activity

Technical discussions with Member States delegates on chemical monitoring issues have been held in the Analysis and Monitoring of Priority Substances (AMPS) working group and the Chemical Monitoring Activity (CMA) in order to arrive at a common view on the necessary monitoring for the WFD. Within that group a guidance document for chemical water monitoring has been prepared (chair German Environmental Agency, Co-chair JRC IES). While the guidance was available at time of the exercise only in draft status, it has been meanwhile adopted by the European Water Directors and been published in early 2009:
Technical Report - 2009 – 025 COMMON IMPLEMENTATION STRATEGY FOR THE WATER FRAMEWORK DIRECTIVE
(2000/60/EC) Guidance Document No. 19 GUIDANCE ON SURFACE WATER CHEMICAL MONITORING UNDER THE WATER FRAMEWORK DIRECTIVE. The Guidance document can be found on the European Commission Information system Circa at:
http://circa.europa.eu/Public/irc/env/wfd/library?l=/framework_directive/guidance_documents/guidance_monitoringpdf/_EN_1.0_&a=d

The ongoing consultation process in the CMA group is important in order to harmonise the approaches and guarantee comparable results, starting from the setting up of the monitoring networks, via the sampling and sample preparation to the chemical analysis. Chemical water analysis is done on routine basis in the Member States according to their national regulations and it is crucial that currently applied approaches will merge into a common strategy which results in comparable assessments throughout Europe.

The method performance criteria for analytical measurements in chemical monitoring have been proposed in the "Draft Commission Directive adopting technical specifications for chemical monitoring and quality of analytical results in accordance with Directive 2000/60/EC of the European Parliament and of the Council". In that draft document an LoQ ≤ 30 % of EQS is required for WFD compliance checking.

2.4 CMA on-site exercise

A first field trial, CMA on-site 1 was organised by JRC IES in 2006 on the Po River in Ferrara, Italy (Comparison of Monitoring Approaches for Selected Priority Pollutants in Surface Water, EUR 22922 EN – 2007). The final report of that event can be found at:
http://ies.jrc.ec.europa.eu/uploads/fileadmin/Documentation/Reports/RWER/EUR_2006-2007/EUR_22922.pdf

Following presentations and discussions within the CMA group, a second field trial was planned within the CMA activities. While the first trial had been limited to 7 invited laboratories, the second CMA on-site event was open to all laboratories nominated through the CMA group. A call for expression of interest in April 2008 to members of the WFD Chemical Monitoring Activity group and a registration deadline on 1.7.08 confirmed the interest of EU Member States to send laboratories for participation.

Similar to the CMA on-site 1 exercise a set of target pollutants was agreed among the participants. Target substances were PBDEs, PAHs, Nonyl- and Octylphenol, specifically selected as their analysis poses particular difficulties at the concentration levels relevant for compliance checking. In order to allow the water sampling in the water column without interference from the river bank, sampling was

performed from bord of two ships. Two ships, the Serbian laboratory ship ARGUS and the Hungarian LEANYFALU have been available.

On 18.9.08 at 8:00 the participants boarded the two ships ARGUS and LEANYFALU, which transferred to the sampling station ca. 10 km downstream of Budapest. On-line measurements and continuous supportive sampling was then started, while participants prepared their equipment. After a detailed briefing on-board, contemporary sampling was performed by all participants at 11:00. An impressive variety of sampling devices was observed.
Every laboratory employed its own approach and tools for this task. In addition to the water samples taken from the River, ampoules with homogenised river water extracts and with standard solutions have been distributed to evaluate the sample preparation and several aspects of instrumental analysis on the analytical procedure.

3 Set-up of CMA on-site 2 event

3.1 Presentations

The introductory part of the CMA on-site event was kindly hosted at the Hungarian Ministry of Environment and Water and opened by Mr. Gyula Holló, Head of the Department of River Basin Management and Water Protection, the Hungarian Water Director. On the first day an intense session of presentations and discussions provided the background for the following practical activities. An update on the latest developments on EU legislation and on the state of EU guidance documents for chemical water monitoring was given. The demanding sampling logistics required then a detailed briefing before the sampling next day on the Danube:

- INTRODUCTION TO WORKSHOP SCOPE AND ORGANISATION, Georg Hanke, JRC IES RWER
- HAZARDOUS SUBSTANCES IN THE CONTEXT OF RISK ASSESSMENT IN THE DANUBE RIVER BASIN, Jaroslav Slobodnik, Environmental Institute
- WATER FRAMEWORK DIRECTIVE – STATE OF THE EQS DIRECTIVE – CMA, Mario Carere, Istituto Superiore di Sanità Italy (Dipartimento Ambiente), CMA chair
- GUIDANCE FOR CHEMICAL MONITORING – STATE OF THE DOCUMENTS, Georg Hanke, Mario Carere, Stefano Polesello JRC IES RWER, ISS, IRSA
- CMA on-site 1, Georg Hanke RWER
- Water analysis for WFD - partitioning and “whole water”, Stefano Polesello, IRSA
- ANALYSIS OF WFD PRORITY POLLUTANTS IN WATER, Presentation and discussion of approaches for PAH, PBDE and Alkylphenols
- BRIEFING FOR SAMPLING AND LOGISTICAL QUESTIONS

The agenda of the event can be found in Annex IV. The presentations from the workshop on 17.9.08 can be found in the DG ENV, WFD public section of CIRCA at:
http://circa.europa.eu/Public/irc/env/wfd/library?l=/framework_directive/chemical_monitoring/cma_on-site/cma_on-site_2/presentations&vm=detailed&sb=Title

3.2 Location selection

In meetings with the Slovak EI Institute and Vituki options and organisation of logistics for CMA on-site 2 have been discussed during preparatory meetings. Options for workshop site and accommodation have also been checked.
The sampling location in the Danube river was selected at ca. 10 km downstream of Budapest on the left river side in 5 m water depth (coordinates: 47.38715° N, 19.01018° E). The ARGUS was anchored and LEANYFALU fastened alongside. A safety boat was at disposal during the water sampling.

3.3 Description of event

The CMA on-site event was planned to bring the discussions that had been held in the AMPS and CMA groups into a practical context. A real monitoring example should show limitations and possibilities on selected examples in current approaches for water monitoring. This experience should help Member States to direct the development of their approaches and to support the finalisation of the CMA guidance document.

After arrival at the sampling site both ships where moored with the bow upstream. The sampling was then started simultaneously by all participants from the bow area of the ships.

For some of the laboratory teams the logistics for sample collection far from their home laboratory was not routine. The laboratory space on-board of ARGUS was therefore at disposal of the participants. The equipment with fume hoods and stainless steel benches allowed the water filtration and solid phase extraction in a clean environment.

3.3.1 Selection of compounds

While the CMA on-site 1 event was aiming at testing the approach, CMA on-site 2 was aiming at laboratories in EU Member States which have a prominent role in the national monitoring programs. In accordance with the participating laboratories a selection of challenging parameters included in the upcoming EQS directive was made. The selection included substance groups that are being analysed routinely and others that are with the WFD for the first time under regulation. The analysis of these compounds in Europe at limits of determination required by the EQS Directive and the method performance criteria in the proposed Draft Commission Directive are no common routine yet. While at time of the CMA on-site event the EQS had been available as proposed values (COM(2006)398), they have meanwhile been adopted as Directive 2008/105/EC, in this report we refer therefore to the Directive:

- **PAH**
- **PBDE**
- **Nonylphenol**
- **Octylphenol**

Environmental Quality Standard values for Inland waters for these substances are:

WFD Polycyclic aromatic hydrocarbons EQS

- Anthracene 100 ng/L
- Fluoranthene 100 ng/L
- Benzo(a)pyrene 50 ng/L
- Benzo(b)fluoranthene + Benzo(k)fluoranthene Σ 30 ng/L
- Benzo(g,h,i)perylene + Indeno(1,2,3-cd)pyrene Σ 2 ng/L

WFD Polybrominated biphenylethers, sum of

- BDE-28
- BDE-47
- BDE-99
- BDE-100
- BDE-153
- BDE-154

EQS Σ 0.5 ng/L

WFD Alkylphenols

- Nonylphenol (NP)
  EQS 0.3 μg/L
- Octylphenol (OP)
  EQS 0.1 μg/L

According to the proposed Draft Commission Directive on Analytical Quality Control, the applied methods should perform with a limit of determination at 30% of the annual average EQS value.

3.3.2 Standard solutions

A set of custom made standard solution in flame sealed brown borosilicate glass ampoules was prepared for PBDE and PAH analysis. Certified standard solutions with different concentrations for the PBDE congeners and PAH where therefore purchased, at concentrations not known to the participants of the exercise. Analysis of these solutions by the participants should show variability of results by instrumental analysis, excluding thus variations deriving from sampling and sample-preparation procedures. For the Alkylphenols a standard solution was prepared by the Italian Institute for Water Research (IRSA).

3.3.3 River water extracts

Variability in analytical results increases when samples contain natural matrix, such as salts, humic acids and other organic macromolecular material. Sample extracts from natural waters should therefore show the result variability when analysing identical samples containing environmental matrix.
During a pre-campaign on 12.6.09 a 300 L filter sample has been taken for extraction and distribution of a homogenised sample with real matrix during CMA on-site 2. For this reason a field filtration manifold was set-up and the water was in-line filtered with a 2” glass fibre filtration cartridge. The

soxhlet extract was diluted, homogenised and aliquots were filled into flame sealed borosilicate brown glass ampoules. For the alkylphenols river water samples have been solid phase extracted, combined, homogenised and then apportioned into ampoules.

3.3.4 Sampling event

The joint sampling of Danube River water was performed on 18.September 2008. A detailed sampling plan was set-up in order to coordinate the various activities that needed to be performed simultaneously or in sequence with > 40 persons on two ships involved. Fig. 1 shows the scheme that was prepared for planning of the event and briefing of the participants. Red bars indicate the sampling events.

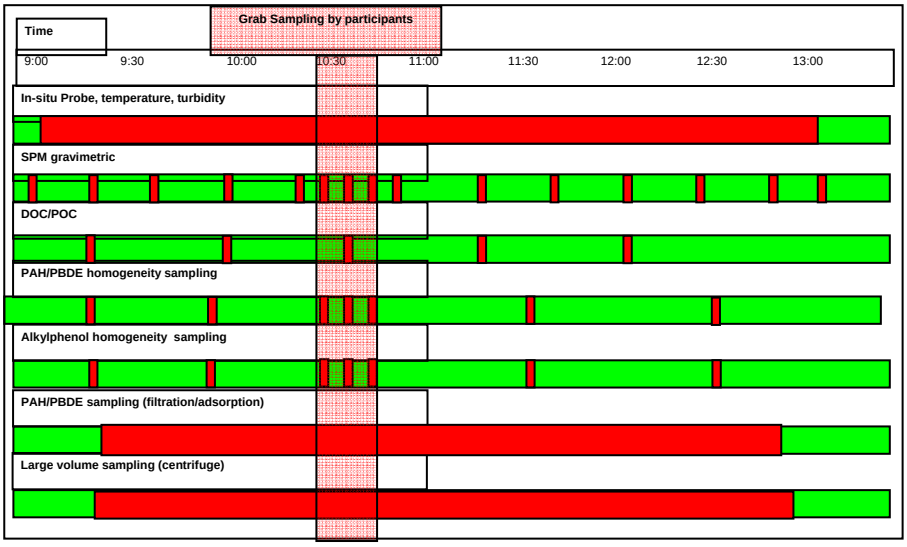

Figure 1: Sampling plan scheme for the CMA on-site exercise

During the execution of the CMA on-site exercise, sampling for the analysis of Suspended Particulate Matter (gravimetric) was done ca. every 10 min and with higher frequency around 11:00. Samples for assessing the homogeneity of the river water where taken at hourly intervals and every 5 min ca. during the joint sampling. Participants sampled simultaneously at 10:55, the duration of the sampling itself was between ca. 5 min and 10 min for the different groups. Large volume sampling was carried out continuously from 10:15 to 13:00 (filtration/absorption) and 11:15-13:00 (centrifuge), respectively.

3.4 Participants

Member States where invited though the CMA group for participation on their own expenses. The invitation was spread also to EU neighbouring countries in order to profit from this occasion also for harmonisation beyond EU. For the result presentation anonymous codes from Lab1 to Lab 27 were attributed to the participants.

Participating laboratories:

Institution name	Institution adress	Country	Participant names	e-mail
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HUN2 South-Transdanubian Environmental, Nature Conservancy and Water Policy Inspectorate	Papnövelde utca 13. H-7621 Pécs	Hungary	Szilárd Molnár Zsuzsa Székely-Diskai	molnar.szilard@freemail.hu szekelynezs@mail.ddkvf.hu
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4 Homogeneity studies

The homogeneity of the distributed standard solutions and sample extracts as well as the homogeneity of the water body during the common sampling procedure were of high importance for the exercise. Homogeneity tests on the ampoules and the river location have been performed during the field trial:

- Test of standard ampoules
- Test of river extract ampoules
- Measurement of SPM concentration
- Repeated measurement of PAH and PBDE concentration

Ampoules with standards and river SPM extracts

4.1 Homogeneity studies for standards

Homogeneity of the prepared ampoules (was tested by analysing 3 randomly selected ampoules prior to shipping. A set of ampoules was retained for further testing in case of necessity. The standard solutions have been purchased from Chiron AS (PAH Standard solution: S-4544-ASS-NO, Batch No. 7682; PBDE Standard solution: S-4545-ASS-T, see Annex III.)

Table 1: PAH standard homogeneity test

PAH Standard [ng/ml]	**Cert. Val.**	S1 A	S1 B	S1 C	Average Standard S2	Stdev	%RSD
Anthracene	**20**	19.9	19.7	19.2	19.6	0.3	1.8
Fluoranthene	**80**	74.2	74.0	73.8	74.0	0.2	0.3
Benzo(a)pyrene	**40**	28.6	27.0	30.5	28.7	1.8	6.1
Benzo(b)fluoranthene	**50**	40.9	40.8	41.5	41.1	0.4	0.9
Benzo(k)fluoranthene	**50**	38.1	36.3	39.3	37.9	1.5	4.0
Benzo(g,h,i)perylene	**40**	35.0	34.4	34.6	34.7	0.3	0.8
Indeno(1,2,3-cd)pyrene	**40**	37.9	37.3	36.5	37.2	0.7	1.9

Table 2: PBDE standard homogeneity test

Standard	**Cert. Val.**	S1 Vial A	S1 Vial A	S1 Vial A	cv %	S1 Vial B	S1 Vial B	S1 Vial B	cv %
[ng/ml]		Repl.1	Repl. 2	Repl. 3	Vial A	Repl. 1	Repl. 2	Repl. 3	Vial B
BDE-28	**10**	9.10	8.67	8.80	2.49	10.01	9.93	10.17	1.24
BDE-47	**40**	33.83	33.58	33.29	0.81	35.15	35.12	36.37	2.00
BDE-99	**60**	50.93	50.56	50.59	0.40	54.49	52.08	53.05	2.27
BDE-100	**15**	13.96	13.87	14.00	0.48	14.27	14.49	14.60	1.17
BDE-153	**10**	9.58	9.36	9.33	1.48	10.52	10.16	10.28	1.76
BDE-154	**10**	9.49	9.09	9.21	2.24	9.75	9.75	9.71	0.25
SUM WFD PBDE	**145**	126.89	125.13	125.22	0.79	134.19	131.53	134.19	1.15

Table 3: Alkylphenol standard S3 homogeneity test

[ng/ml]	S3 Vial A	S3 Vial B	S3 Vial C	S3 Vial D	S3 Vial E	S3 Vial F	S3 Vial G	S3 Vial H	Average	STDEV	STDEV %
4-nonylphenol	570.6	625.1	590.1	654.5	628.6	624.9	612.6	605.3	614.0	25.7	4.2

The homogeneity of the standard solutions was tested for PAH as well as for PBDE on selected ampoules. Variation coefficients, below 7 % for all compounds, were consistent with the variability achievable with the instrumental analysis, proving the homogeneity of the distributed standards.

4.2 Homogeneity studies for extracts

Also the homogeneity of the prepared ampoules with the extract from a filter cartridge loaded with SPM from ca. 300 L Danube River water was tested by analysing a set of randomly selected ampoules prior to shipping.

Table 4: PAH extract homogeneity test

Extract E1 [ng/ml]	E1 A	E1 B	E1 C	Average Extract E1	Stdev	%RSD
Anthracene	5.7	5.6	6.1	5.8	0.2	3.9
Fluoranthene	57.7	55.3	61.0	58.0	2.9	4.9
Benzo(a)pyrene	19.8	19.4	20.3	19.8	0.4	2.2
Benzo(b)fluoranthene	28.1	28.6	31.5	29.4	1.8	6.2
Benzo(k)fluoranthene	9.7	9.5	10.5	9.9	0.5	5.2
Benzo(g,h,i)perylene	16.8	16.5	17.3	16.8	0.4	2.3
Indeno(1,2,3-cd)pyrene	16.9	16.3	17.0	16.8	0.4	2.2

Table 5: PBDE extract homogeneity test

PBDE Extract	E1	E1	E1	Average	cv%
[ng/ml]	Vial A	Vial B	Vial C		
BDE-28	<0.0023	<0.0019	<0.0039	n.d.	n.d.
BDE-47	0.100	0.100	0.114	0.105	7.81
BDE-99	0.167	0.190	0.165	0.174	8.15
BDE-100	0.033	0.037	0.039	0.036	8.42
BDE-153	0.021	0.021	<0.014	0.021	0.86
BDE-154	0.017	0.020	0.019	0.019	9.95
Sum WFD PBDE	0.337	0.368	0.336	0.347	5.22

Table 6: Alkylphenol extract homogeneity test

[ng/ml]	E2 Vial A	E2 Vial B	E2 Vial C	E2 Vial D	E2 Vial E	E2 Vial F	E2 Vial G	Average	STDEV	STDEV %
4-nonylphenol	339.1	370.2	332.9	342.2	363.8	374.6	370.2	356.1	17.4	4.9

Matrix loaded samples show only slightly increased variability in the PAH and PBDE measurements with an coefficient of variability of below 10 %. The measurements therefore confirmed the homogeneity of the distributed sample extracts.

4.3 Homogeneity of river water

Sampling was performed at a large river, including thereby all sources of variation, also the sampling itself, into the comparison. The homogeneity of the river water body during the sampling event had therefore to be shown. The amount of total suspended matter at a high frequency and the target analytes where measured repeatedly.

4.3.1 Suspended particulate matter

Suspended particulate matter was determined gravimetrically according to measurement standard: MSZ 12750-6:1971 3.)

Table 7: Suspended particulate matter concentration during the sampling period (VITUKI)

Time [hh:mm]	10:15	10:25	10:35	10:45	10:55	11:00	11:03	11:05	11:09	11:12	11:22	11:45
SPM [mg/L]	5	8	8	8	6	6	8	8	10	10	9	11

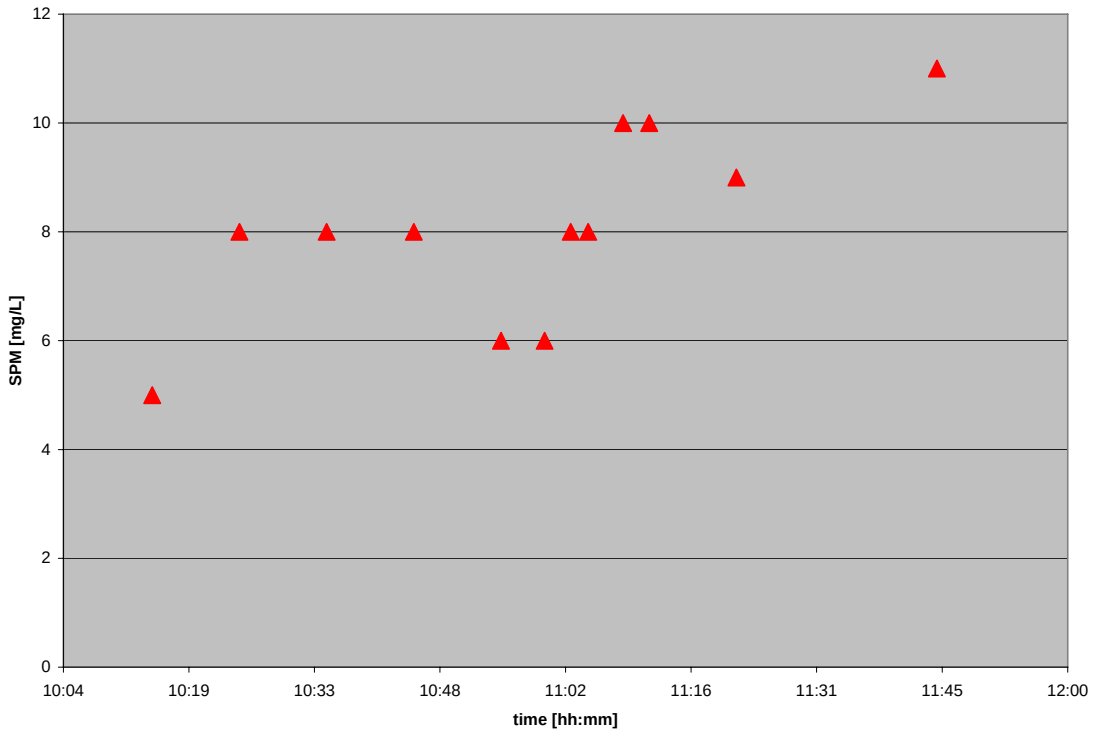


Figure 2: Suspended particulate matter concentration in water samples during sampling period

The concentration of suspended particulate matter varied between 6 and 10 mg/L in the sampling period. The measured SPM values are expressed at +/- 1.0 mg/L, which is thus in the range of the measured variability. It is interesting to note that the average SPM concentration as estimated from the dry weight of the SPM obtained from the centrifuge (25,4 g in the time from 11:15 to 13:00) divided by the total water volume processed (1810L) is somewhat higher with 14 mg/L. However, the sampling periods did not exactly match, which makes a direct comparison here difficult.

Table 8: Dissolved Organic Carbon concentration during the sampling period (VITUKI)

Time [hh:mm]	10:25	10:45	11:03	12:10	12:55
DOC [mg/L]	2.14	1.90	2.03	2.01	1.93

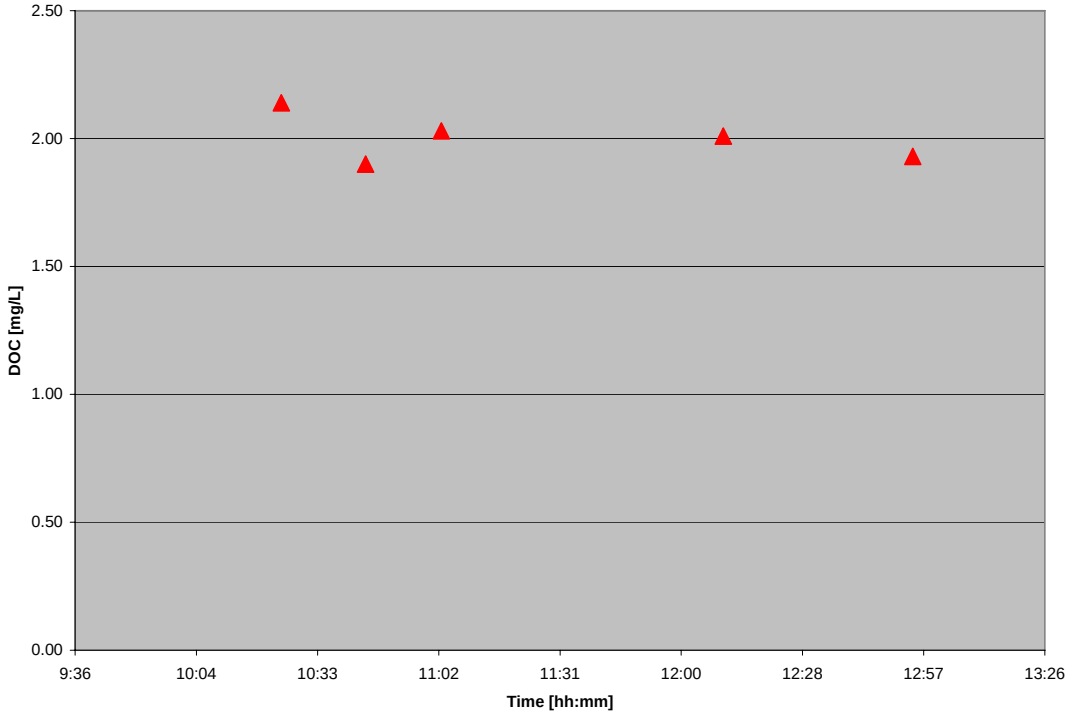


Figure 3: Dissolved Organic Carbon concentration in water samples during sampling period

The concentration of Dissolved Organic Carbon varied very little, with a standard deviation of 0.1 mg/L and indicates thus homogeneity of the River water.

4.3.2 Homogeneity of PAH in river water

Table 9: PAH concentrations during sampling period

Time [hh:mm]	10:20	10:45	10:55	11:03	11:10	12:15	12:55
[ng/L]							
Anthracene	0.88	0.59	0.44	0.49	0.45	0.82	0.46
Fluoranthene	4.25	4.11	3.17	3.29	2.72	4.54	2.88
Benzo(a)pyrene	1.05	1.11	0.68	0.79	0.56	0.97	0.57
Benzo(b)fluoranthene	1.78	1.82	1.28	1.43	0.96	1.74	1.03
Benzo(k)fluoranthene	0.64	0.69	0.44	0.50	0.32	0.60	0.33
Benzo(g,h,i)perylene	1.21	1.05	0.80	0.90	0.63	1.05	0.62
Indeno(1,2,3-cd)pyrene	1.15	1.04	0.82	0.90	0.62	1.03	0.61

The test for homogeneity of the river water concerning PAH concentrations shows during the contemporary sampling by the participants from 10:55 to ca. 11:10 no indication for a significant inhomogeneity in PAH concentration which will have to bee seen in relation to the results of the participants.

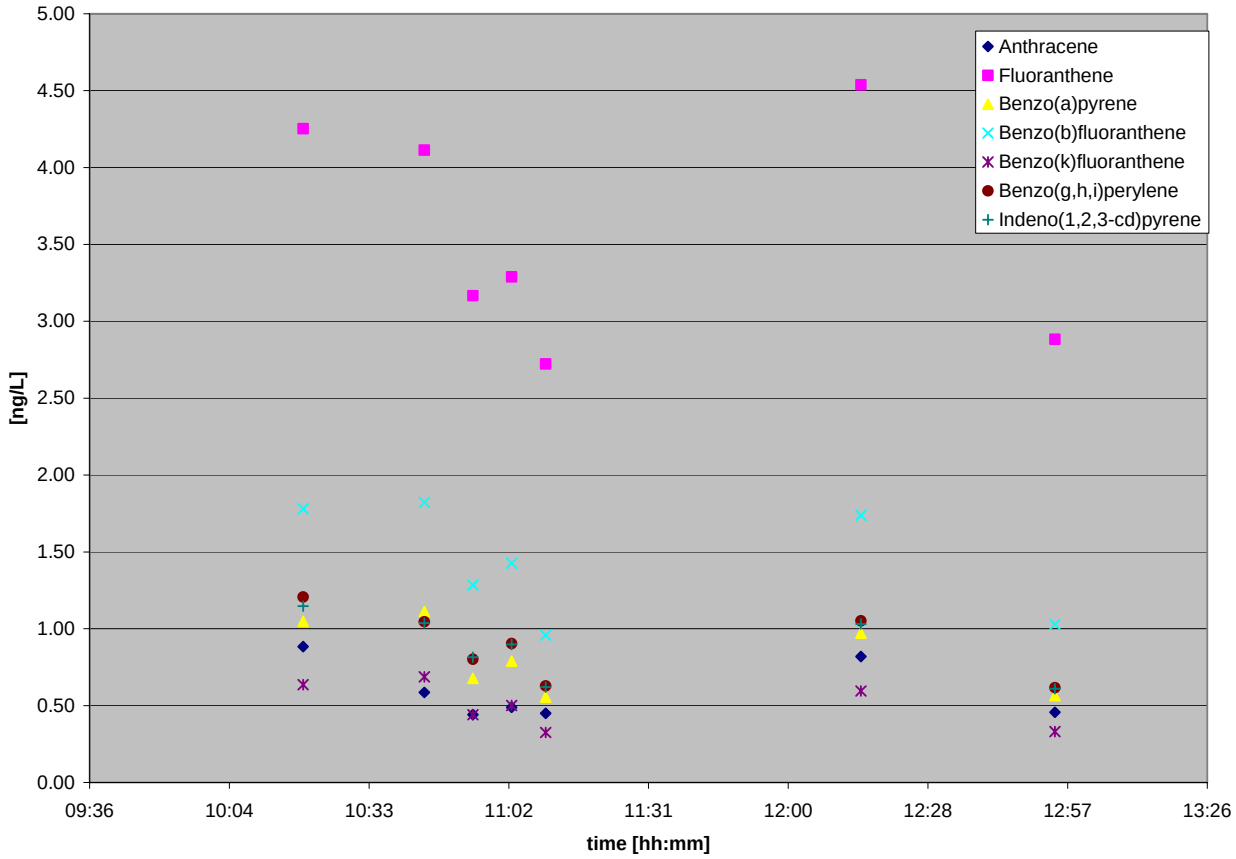


Figure 4: PAH concentration in water samples during sampling period

4.3.3 Homogeneity of PBDE in river water

Table 10: PBDE concentrations during sampling period

Time [hh:mm]	10:20	10:45	10:55	11:03	11:10	12:15	12:55
PBDE [ng/L]							
BDE-28	0.0013	0.0007	0.0009	0.0009	<0.0003	0.0007	0.0009
BDE-47	0.0347	0.0202	0.0271	0.0239	0.0129	0.0187	0.0111
BDE-99	0.0420	0.0287	0.0308	0.0288	0.0131	0.0206	0.0106
BDE-100	0.0116	0.0070	0.0095	0.0072	0.0030	0.0058	0.0030
BDE-153	0.0096	0.0085	0.0099	0.0089	0.0069	0.0059	0.0057
BDE-154	0.0055	0.0051	0.0061	0.0048	0.0027	0.0030	<0.0012

A significant decrease of ca. 50 % is shown in the sampling point 11:10 compared to the previous one. Nevertheless the sampling by the participants was finished within 10 min, i.e. at ca. 11:05. While being of high importance for further discussions on variability of contaminant concentrations in surface waters we assume that this decrease did not influence the overall variability within this exercise.

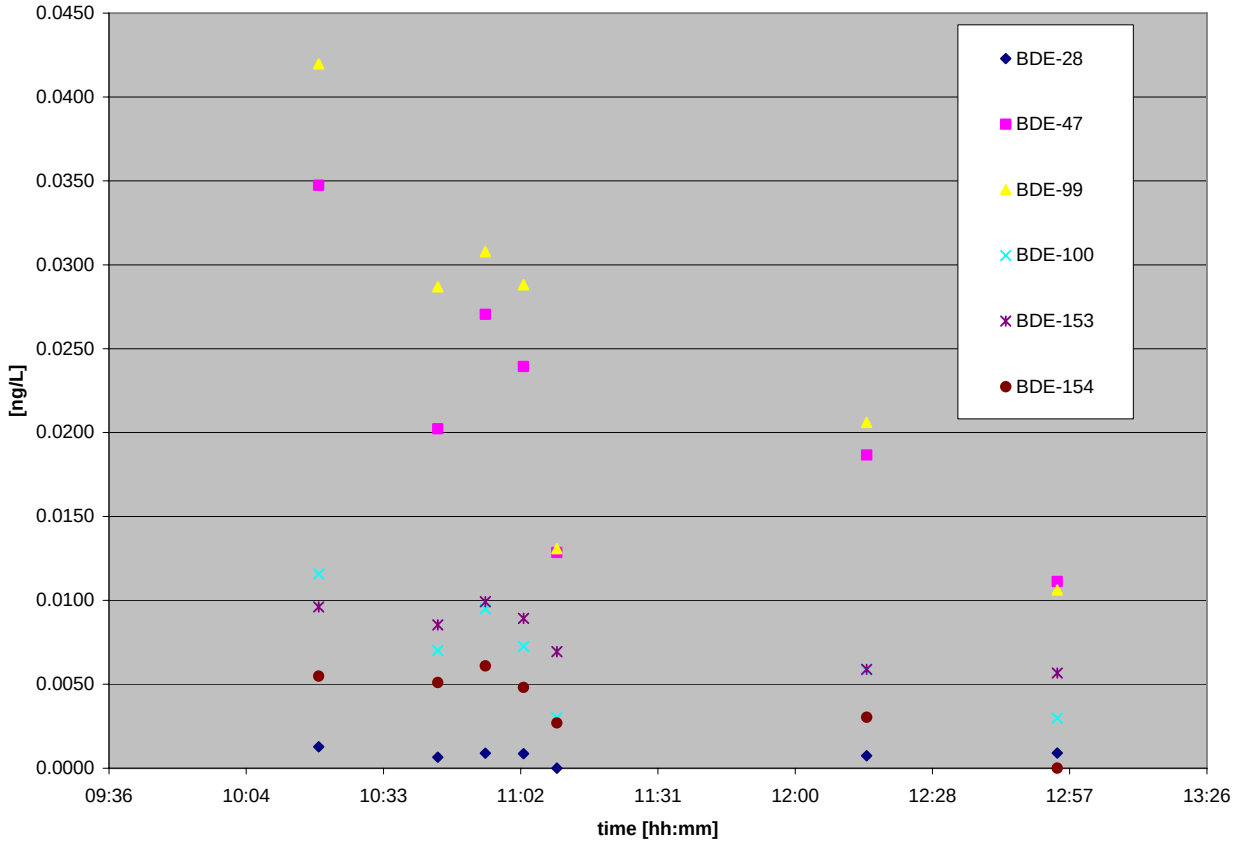


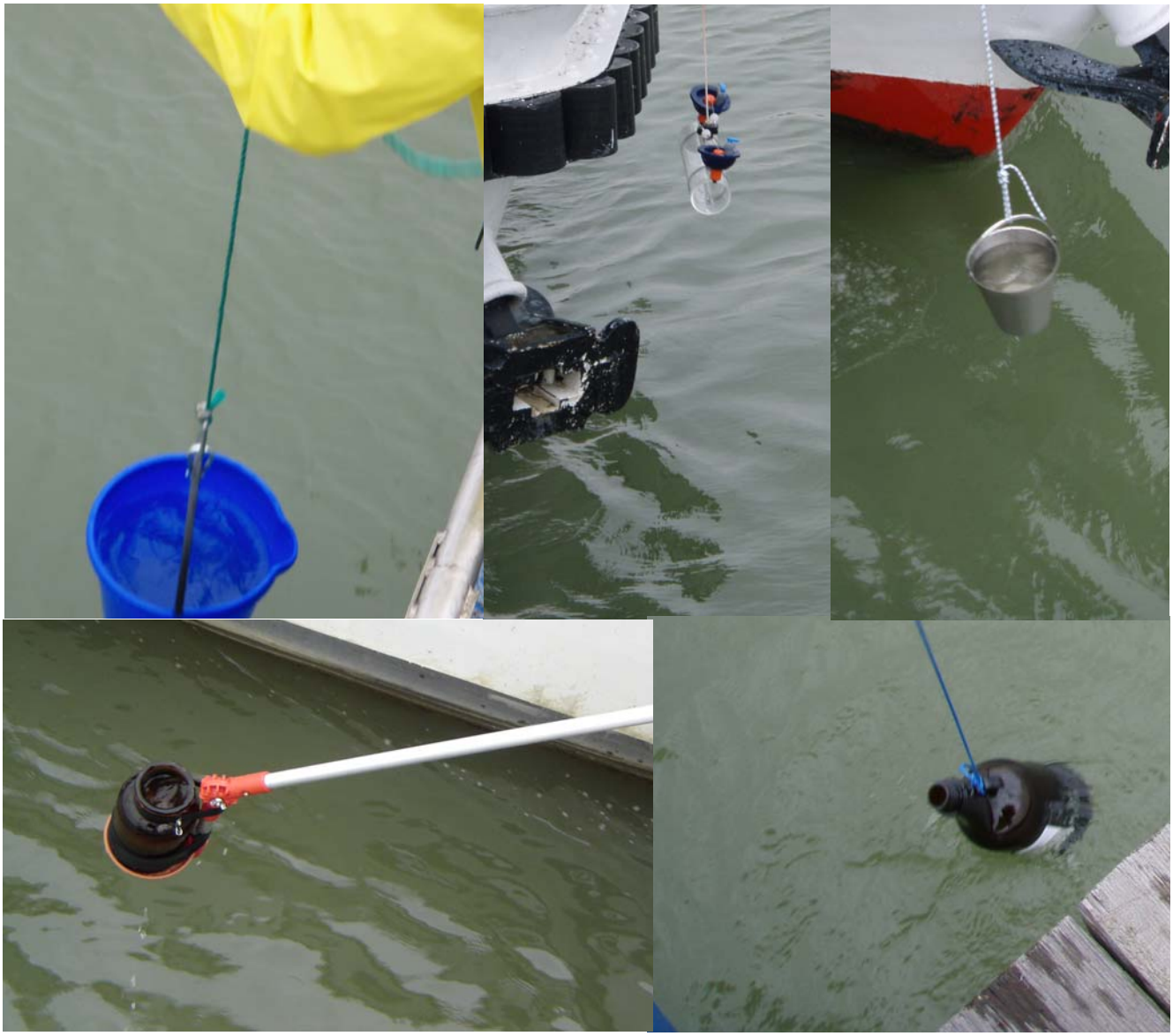
Figure 5: WFD PBDE in river water samples during sampling period

5 Approaches for water monitoring

5.1 Methods employed by participating laboratories

A wide range of approaches has been applied by the participants: Samples were taken directly with a bottle, with a steel or plastic bucket or a dedicated sampler and then transferred to bottles. Another approach was the sampling of particulate matter with a flow-through centrifuge. As sample containers for water samples mostly used solvent bottles or borosilicate glass bottles have been employed.
A few groups extracted their samples on-site with solid phase extraction, while most participants send their samples with a courier service to their home laboratories.

Numerous approaches have been employed for collecting of the samples from the Danube River:



5.2 Methods employed by JRC IES:

The CMA on-site team from the JRC IES laboratory employed two methods, aiming thus at a broad coverage of sampling and analytical methods. This method array should provide results obtained by different methodologies, comparing thus techniques that use a different principle of particle separation and extraction. Most of the methods were aiming at separation between the dissolved and the particle bound pollutant fractions. While this separation is clearly an operationally defined one, it allows comparison of results under application in a real water body.

45 L GF/F filtration + 2 x 50 g XAD
In parallel to other methods also the filtration in combination with adsorptive extraction of a medium size sample was used. With the XAD column containing 50 g adsorbent these columns are suitable for extraction of up to ca. 300 L water in inland surface water bodies.

2 L liquid/liquid extraction
This method was used for homogeneity tests. It does not allow separation of particulate and dissolved contaminant fraction. It is questionable whether contaminants on particles can be monitored under all circumstances, e.g. when the substances are trapped in particles with a hydrophilic cover. The use of Dichloromethane for liquid /liquid extraction of water as routine method is not recommended due to the problematic disposal of wastewater contaminated with this chlorinated solvent.

6 Results

A tentative deadline for result submission on 30.11.08 was set and respected by most participants. A reporting sheet template for collecting both analytical data and information about the applied methodologies was distributed to the participants. Some problems in reporting occurred due to the change in the sequence of reporting for some PBDE congeners. These errors have been corrected as they would have otherwise biased mainly the outcome of the exercise. Not all laboratories reported results for all parameters. While this exercise required reporting of specific information not always asked in analytical reports, the reporting of metadata such as details of the analytical approaches and systems used as well as information about the data quality, as e.g. uncertainty proved to be very inhomogeneous.

6.1 PAH results from participating laboratories

6.1.1 PAH standard results

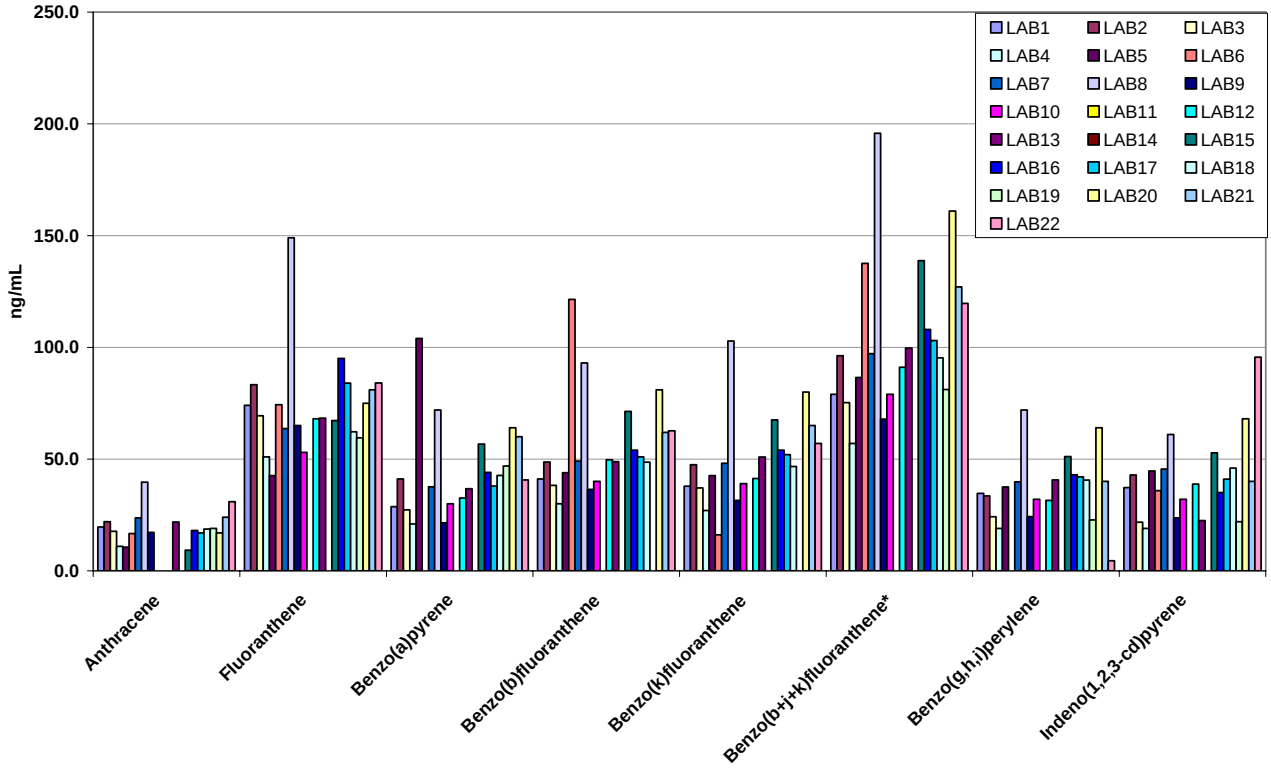


Figure 6: PAH Standard S2 results

The analysis of the PAH standard solution resulted in average in a relative standard deviation of 38 % (range 30 – 45 %RSD for single PAHs) (see figure 9). No compound specific bias can be observed,

while it is shown that one laboratory (Lab 8) reports data which are for most compounds too high with a factor of ca. 2.
The certified concentrations can be found in table 2 and the standard certificate in the Annex III.

6.1.2 PAH extract E1 results

As expected, the result for the matrix loaded Extract sample introduced a higher variability among the results. As this sample cannot be linked to a standard and an externally assigned value could not be derived, a comparison could only be made between the participating laboratories. Variability in analysis from a single laboratory was shown in the homogeneity study performed by JRC, leading to a relative standard deviation of 2 to 6 % of single PAHs in the Extract after 3 replicates. This shows, also in comparison with the previous result for a standard solution, that the added matrix is a major source of variability.

The increased relative standard deviation ranging from 35 to 70 % (see figure 7), indicates that this exercise added complexity compared to the standard. Both approaches, the direct introduction of a matrix loaded sample as also the clean-up introduce additional variability into the analytical procedure.

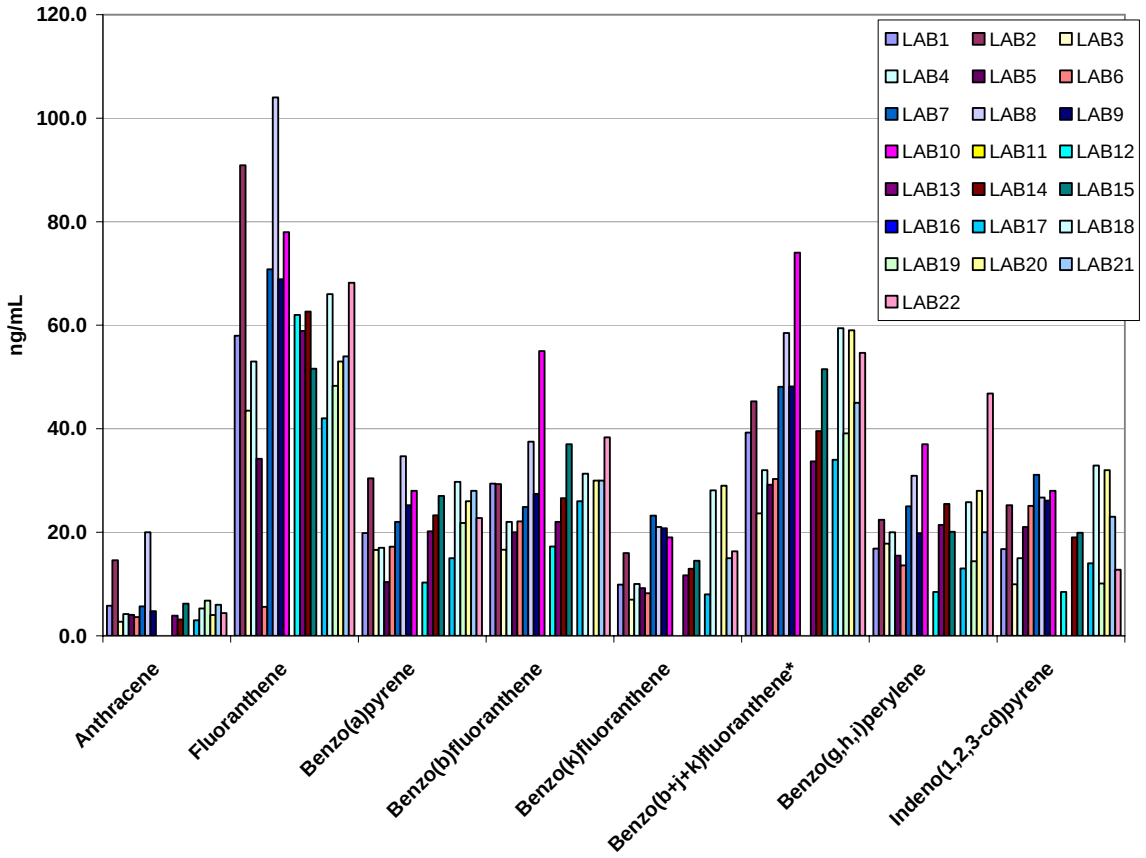


Figure 7: PAH Extract E1 results

No compound specific bias could be observed. Variability is higher, but no evident outliers have been reported.

6.1.3 PAH River Danube results

The main aim of the CMA on-site exercises is to compare the final results of environmental analysis performed at the same location, according to available, current protocols in view of WFD compliance checking. For PAH analysis in the Danube River water, 21 participants reported results.

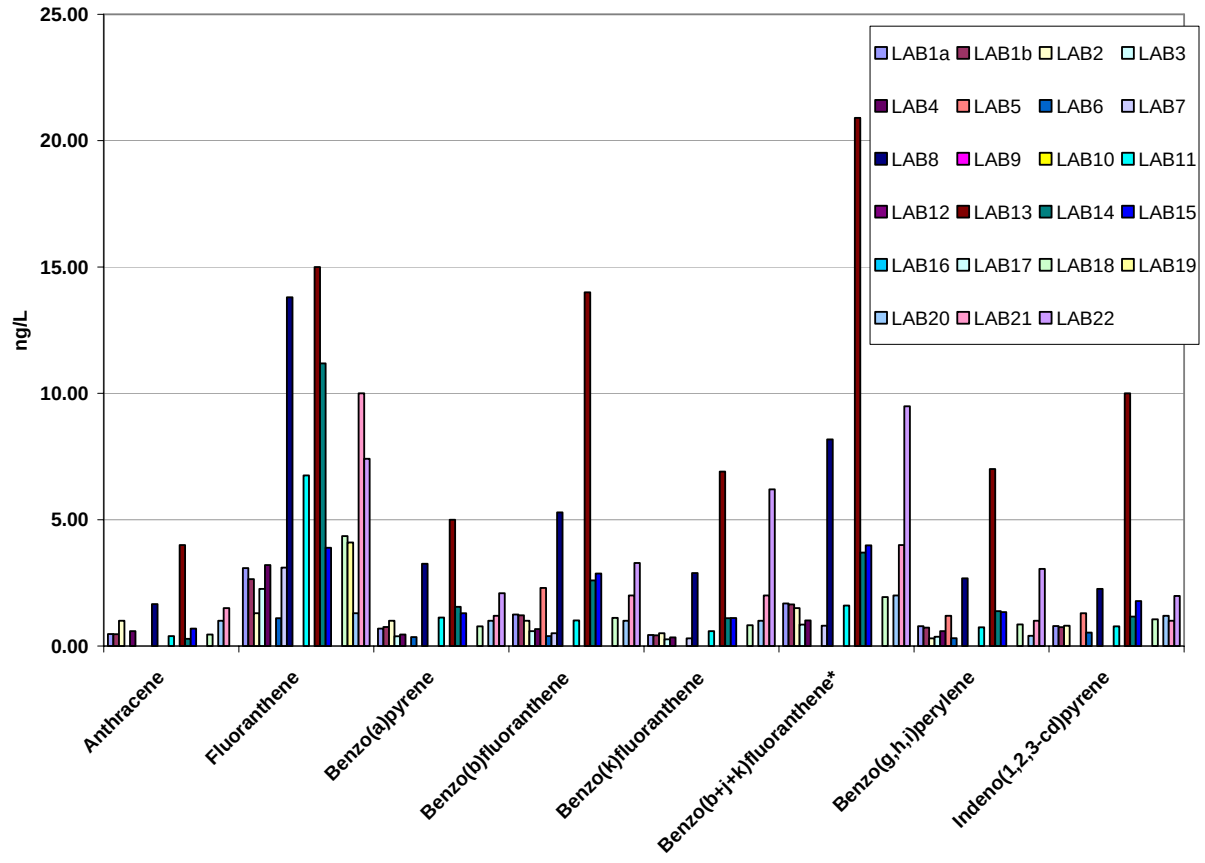


Figure 8: PAH whole water results

The results are shown in Figure 8 and show, compared to standard and extract analysis, a inhomogeneous picture. Lab 13 and Lab 22 report high values compared to other laboratories. We verified that the outlier values of Lab 13 are due to calculation errors, however, data corrections were not accepted after results presentation to participating laboratories.

6.1.4 Variability in PAH results

The difference in the observed relative standard deviation RSD for the different sample types is shown here and also for other compounds in "target plots". The three compartments of the ring (green for analysis of the standard solution, orange for the extract and red for the river water analysis) demonstrate the relation of the RSD for the different sample matrices. As expected, the RSD increases with the sample complexity. The relation of the RSDs varies for different analyte groups.

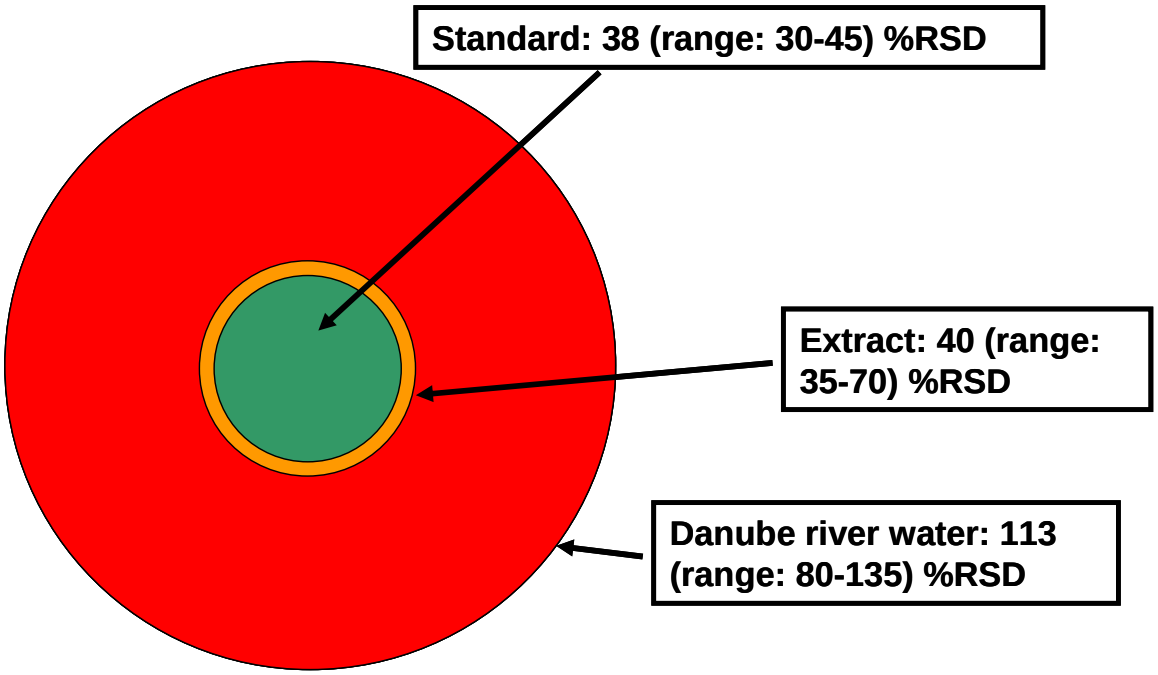


Figure 9: Variability of reported PAH results in standard, homogenised extract and Danube river water. Results are average relative standard deviations for all PAHs and in brackets the range for single PAHs

It is evident from the presentation in figure 9 that the majority of the variability observed in the reported PAH results for the Danube river water was due to issues related to the processing of real environmental samples, such as the sampling approach and sampling technique and not because of variabilities in laboratory calibration or difficulties due to matrix effects or clean-up procedures. Almost all of the 22 laboratories delivered results for PAH in the standard solution and the homogenised extract, respectively, whereas 4-5 of these laboratories had results below LOQ for some PAHs in the Danube river water. The PAH concentrations in the standard solution and homogenised extract were at comparable levels. Average concentrations of Benzo(g,h,i)perylene and Indeno(1,2,3-cd)pyrene in the Danube river water were at EQS levels and a factor of 20-100 times below EQS for all other PAHs, suggesting that WFD compliance monitoring is challenging but feasible.

6.1.5 Methods performance for PAH WFD monitoring

Figure 10a: Number of laboratories that are ready (green) or not ready (red) for the sensitivity requirements of 30% EQS as specified in the proposal for a Commission Directive on technical specifications for chemical analysis and monitoring of water status for WFD chemical monitoring.

Of the 17 laboratories that reported LOQs only 7 have reported LOQs that comply with the 30% EQS requirements as foreseen in the proposal for a Commission Directive on technical specifications for chemical analysis and monitoring of water status. However, all the 10 laboratories considered "not ready" in figure 10a are in fact ready for 5 out of the monitored 7 PAHs in this exercise (see figure 10b).

Figure 10b: Number of laboratories that are ready (green) or not ready (red) for the sensitivity requirements of 30% EQS as specified in the proposal for a Commission Directive on technical specifications for chemical analysis and monitoring of water status for Anthracene, Flouranthene, Benzo(a)pyrene, Benzo(b)fluoranthene, and Benzo(k)fluoranthene WFD monitoring.

The problem with insufficient sensitivity for these 10 laboratories is for Benzo(g,h,i)perylene and Indeno(1,2,3-cd)pyrene only, for which a low EQS of 2 ng/L for the sum of these 2 PAHs is defined (Directive 2008/105/EC). It is important to note that the EQS for Benzo(b)fluoranthene and Benzo(k)fluoranthene as well as for Benzo(g,h,i)perylene and Indeno(1,2,3-cd)pyrene, respectively, are in fact sums of two PAHs whereas in chemical analysis these compounds are analysed separately and have separate LOQs. However, in the proposed Commission Directive it is not defined how to derive the required sensitivity (LOQ) for a single analyte when the EQS is expressed as a sum of two or more substances. It would seem logic to require a LOQ lower than 0.3* the EQS of a sum of substances for every single analyte. Nevertheless, in the absence of a requirement in the proposed Commission Directive to derive lower LOQs in case of EQS for a sum of substances, we considered for this exercise the required LOQ as 30% of the EQS of the sum for each single substance, i.e., an EQS for the sum of Benzo(g,h,i)perylene and Indeno(1,2,3-cd)pyrene of 2 ng/L leads to a required LOQ of 0.6 ng/L (and in fact requiring a 2 times lower LOQ would not have changed the number of "ready" laboratories participating to this exercise).

6.2 PBDE results from participating laboratories

The analysis of PBDE in environmental water samples is still challenging. This is reflected in the smaller number of laboratories returning results for this analyte group. In preparation of the WFD implementation methodologies have been developed or adjusted that allow laboratories to analyse these compounds. Also an EPA standard method (EPA1614: Brominated Diphenyl Ethers in Water Soil, Sediment and Tissue by HRGC/HRMS of August 2007) is meanwhile available.

6.2.1 PBDE Standards S1 results

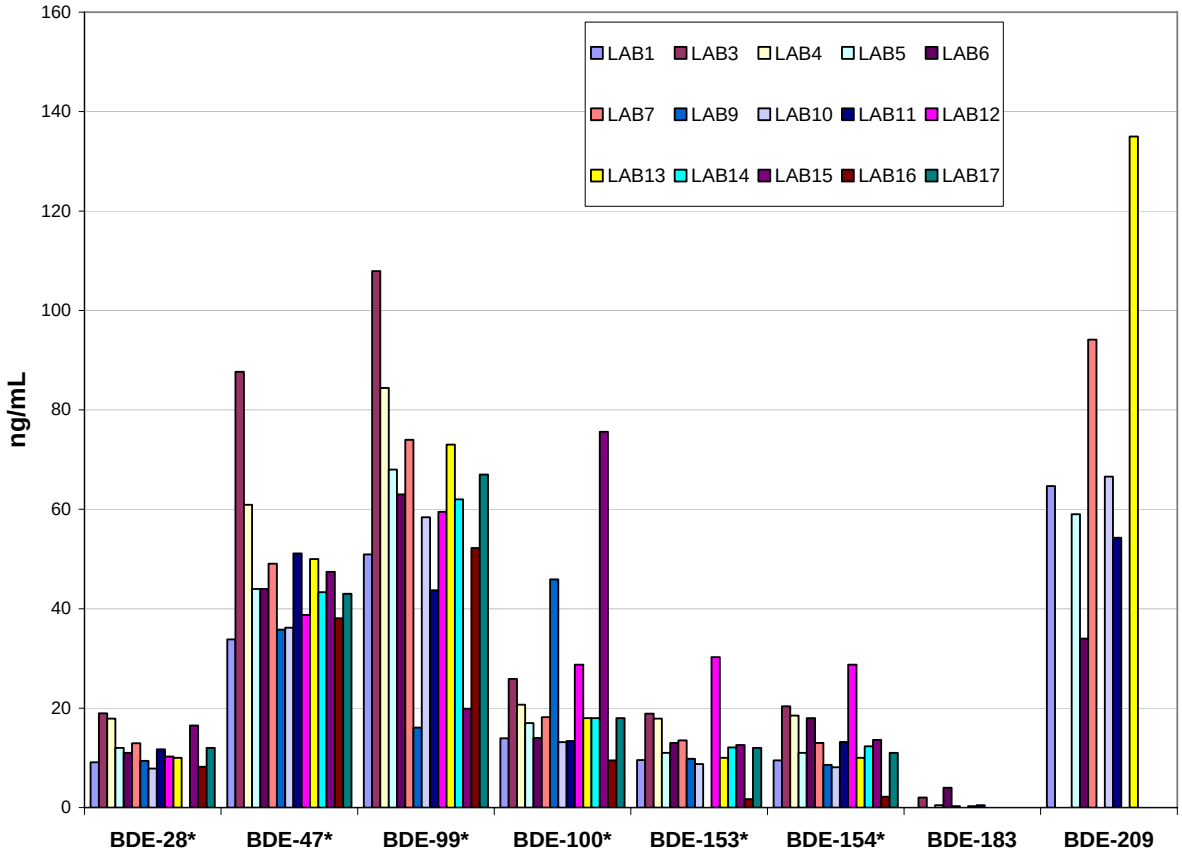


Figure 11: PBDE Standard S1 results

14 laboratories reported results for the analysis of the PBDE standard solution. The detailed results can be found in the Annex II. Figure 11: PBDE Standard S1 resultsAlso PBDE congeners not regulated currently under the WFD (BDE-183, BDE-209) had been considered in the CMA on-site 2 exercise but could not be evaluated further in the current report.
The concentrations of PBDE congeners in the standard solution can be found in table 2 and the certificate for the standard solution in Annex III.

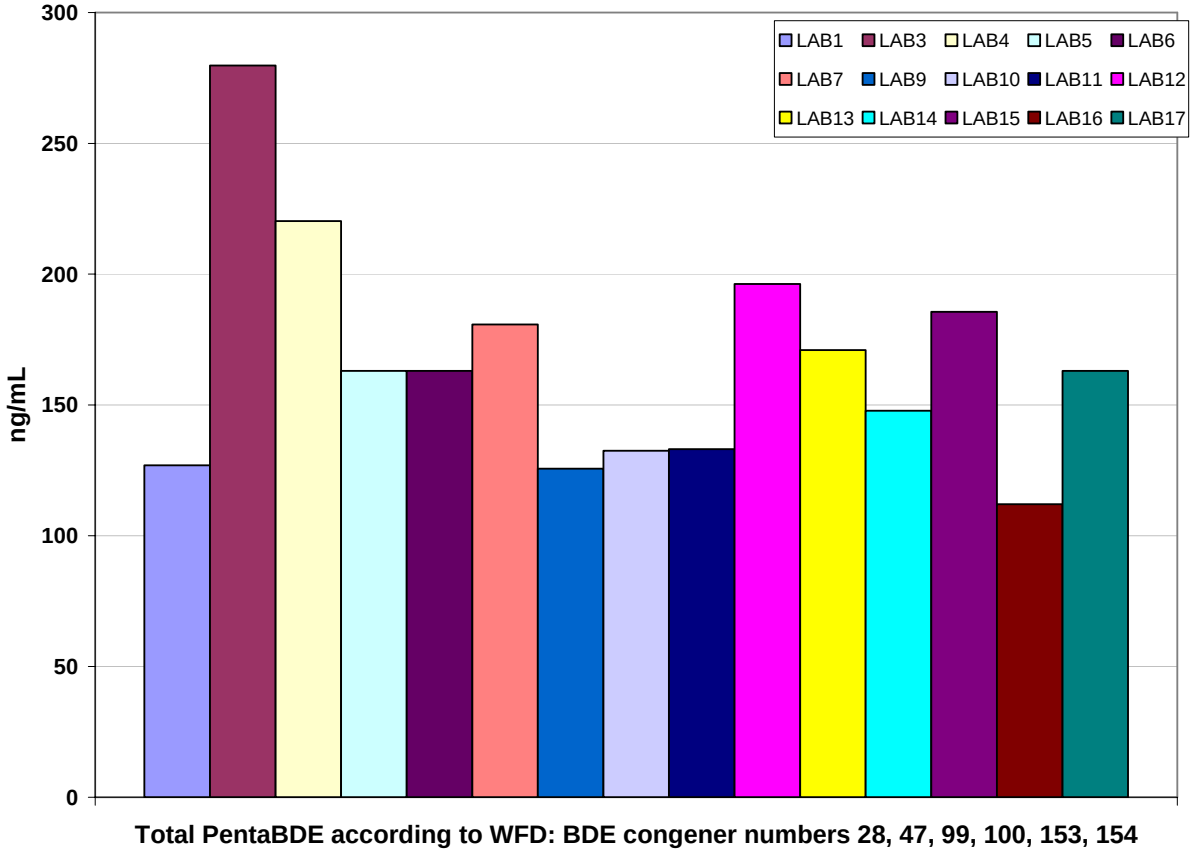


Figure 12: PBDE Standard S1 sum WFD PBDE results

Figure 12 shows the sum of PBDE congeners as relevant for the Penta-PBDE group regulated under WFD.

6.2.2 PBDE Extract E1 results

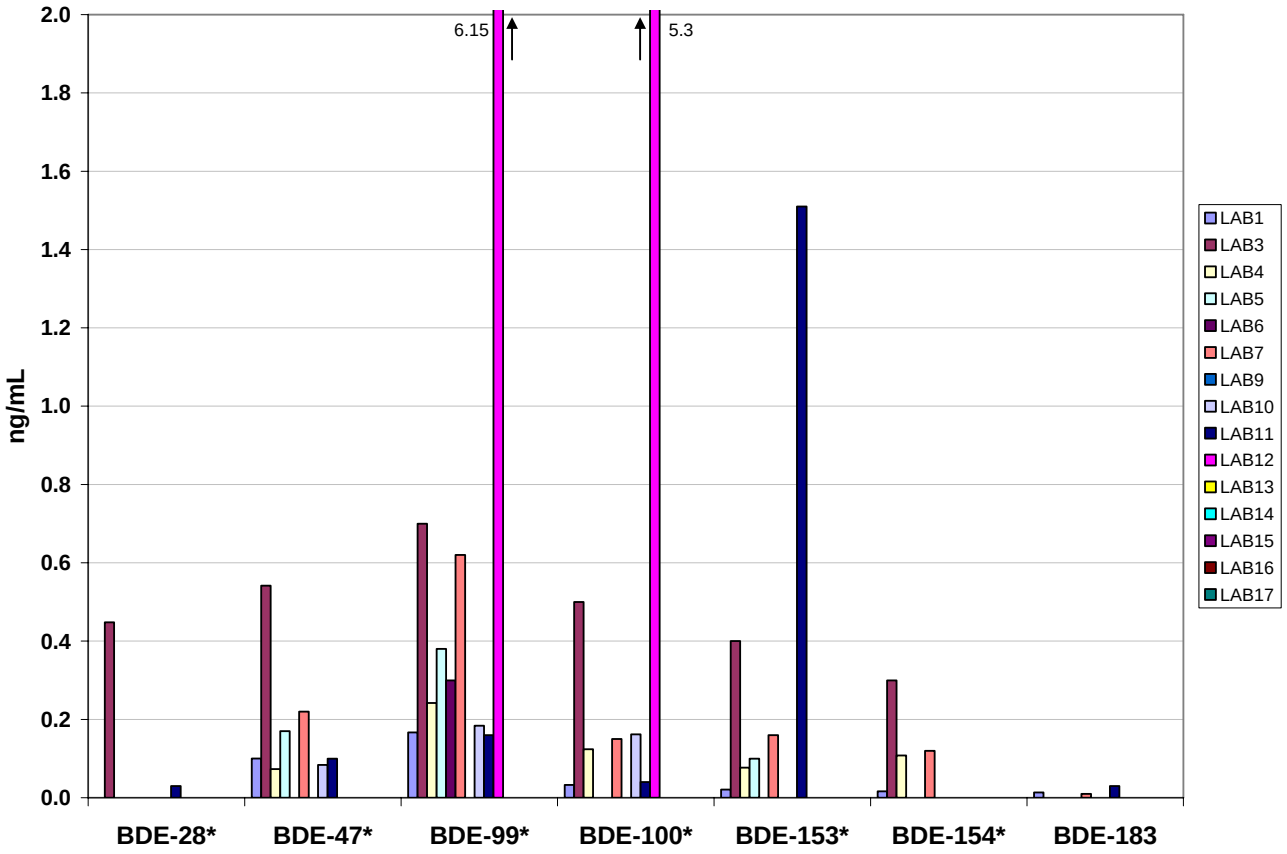


Figure 13: PBDE Extract E1 results

As evident in the graph with the results of the Extract E1 analysis in Figure 13, the additional matrix makes the analysis more difficult. Much less laboratories have reported results and the pattern of the reported concentrations varies considerably between participants.

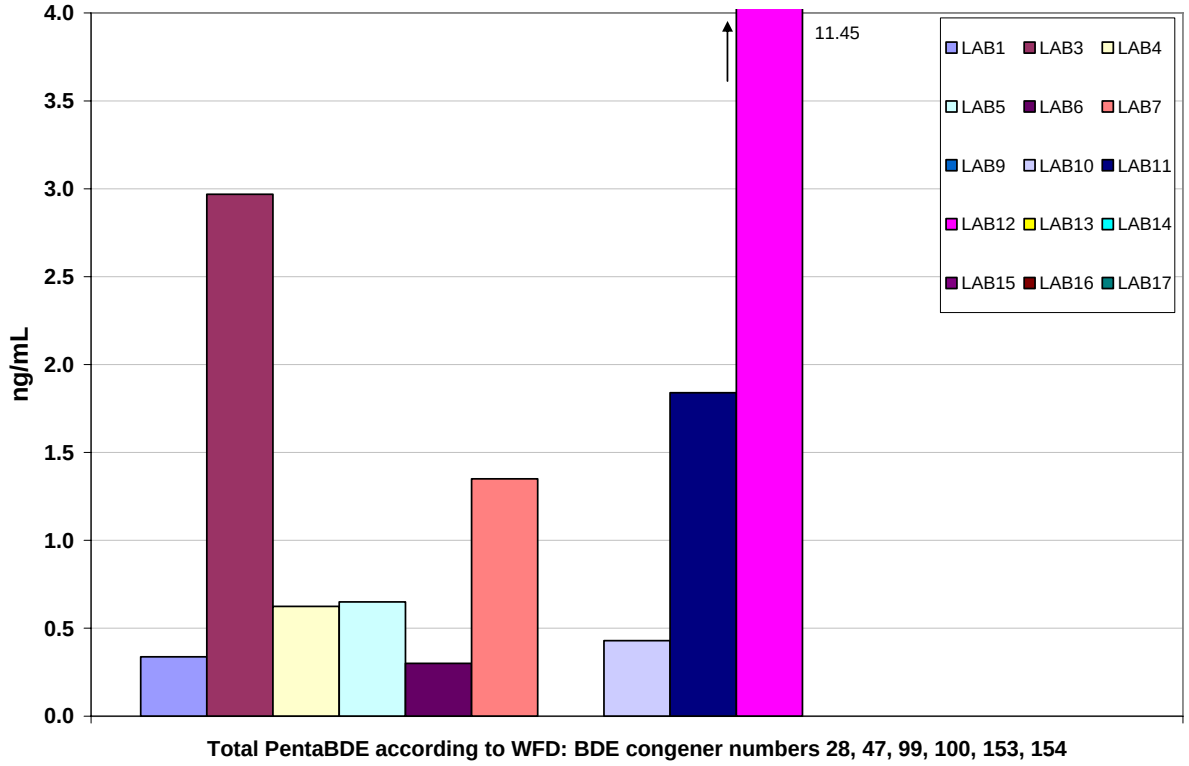


Figure 14: PBDE Extract E1 sum WFD PBDE results

Also the sum of WFD PBDE shown in figure 14 shows a much higher variability compared to the standard for PBDE shown in figure 12.

6.2.3 PBDE Danube river results

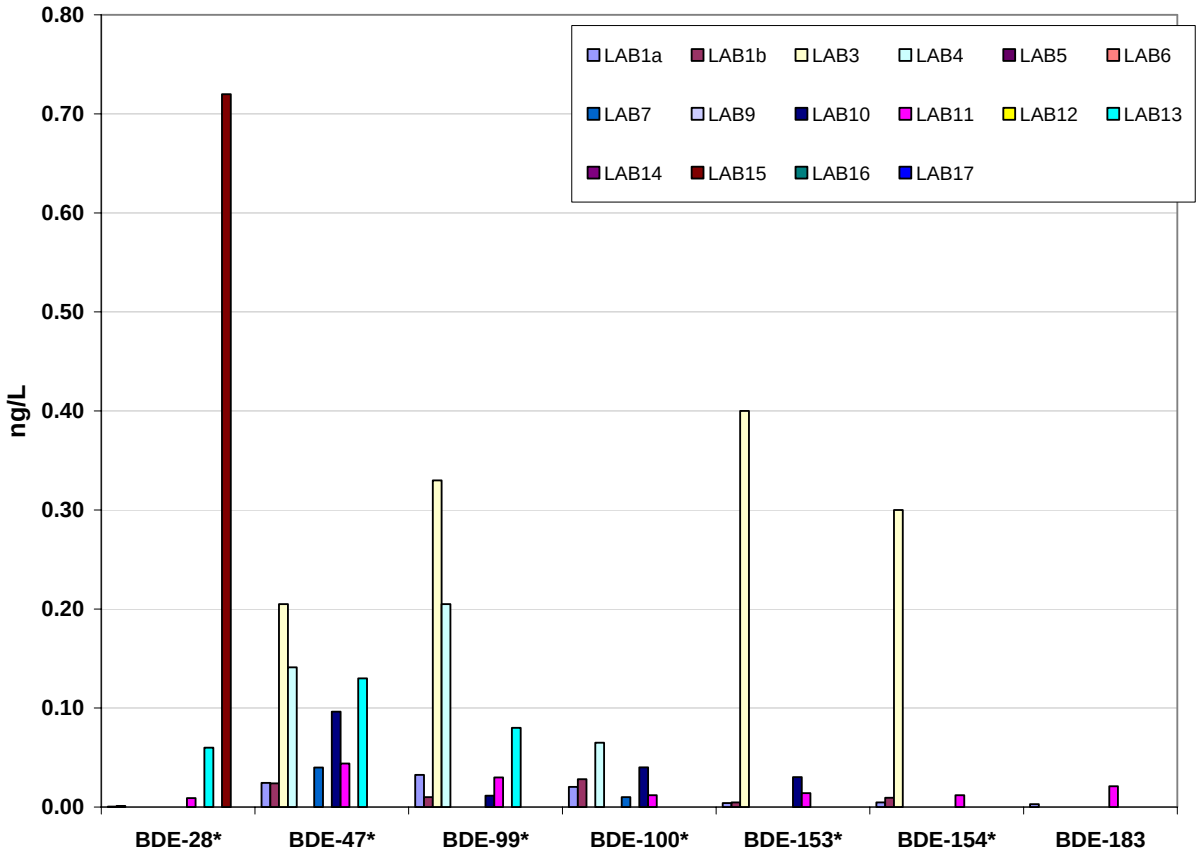


Figure 15: PBDE whole water results

The detailed results for single congeners, Figure 15, shows an even higher variability of the reported concentrations. The results shown for Lab 1a + 1b (JRC) indicate two different methodologies employed.

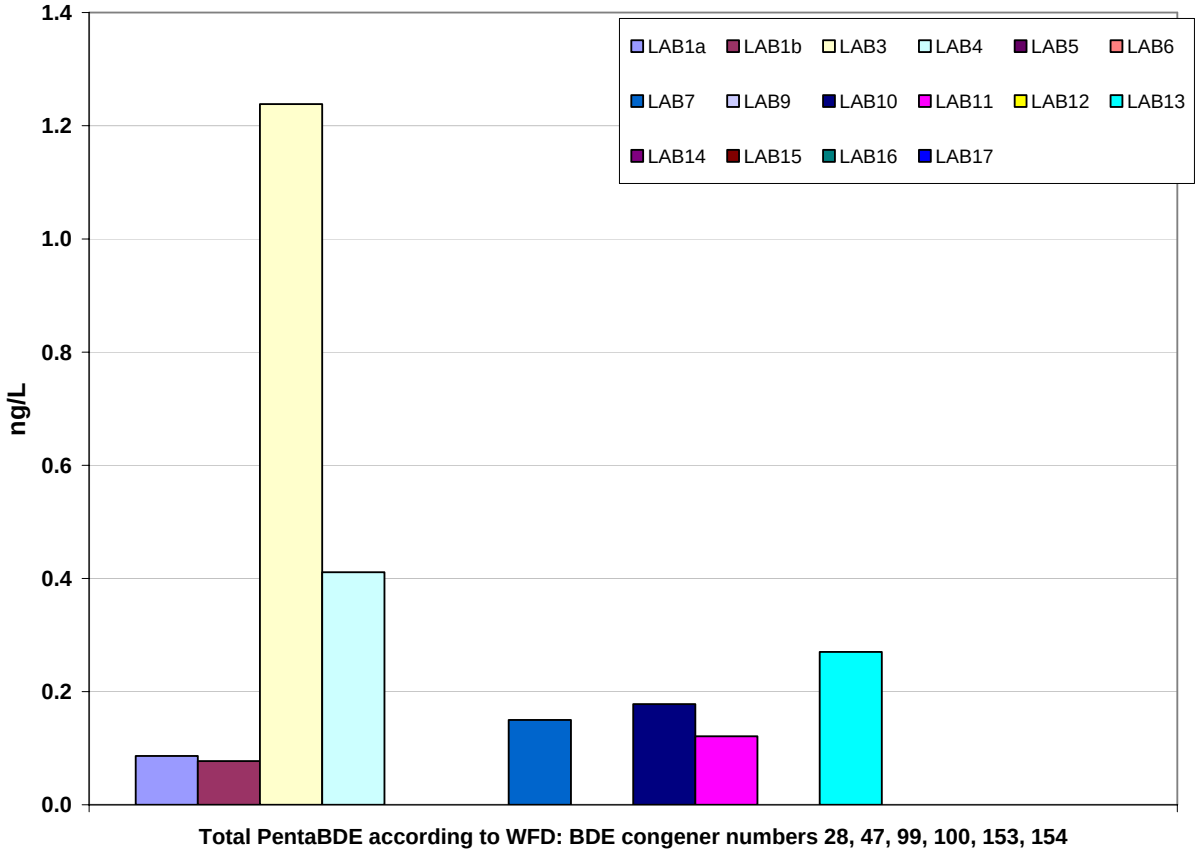


Figure 16: PBDE sum whole water results

In Figure 16 combined congener results are shown as a sum of WFD PBDE congeners in whole water analysis. With a proposed annual average limit value of 0.5 ng/L the quantification limit for the sum of PBDE should be at 0.3 of that value, according to the proposed analytical method performance criteria. A required quantification limit for the PBDE sum of 0.15 ng/L would result. The results indicate that a thorough control of blanks and data quality is important in order to show compliance with WFD EQS requirements.

6.2.4 Variability in PBDE results

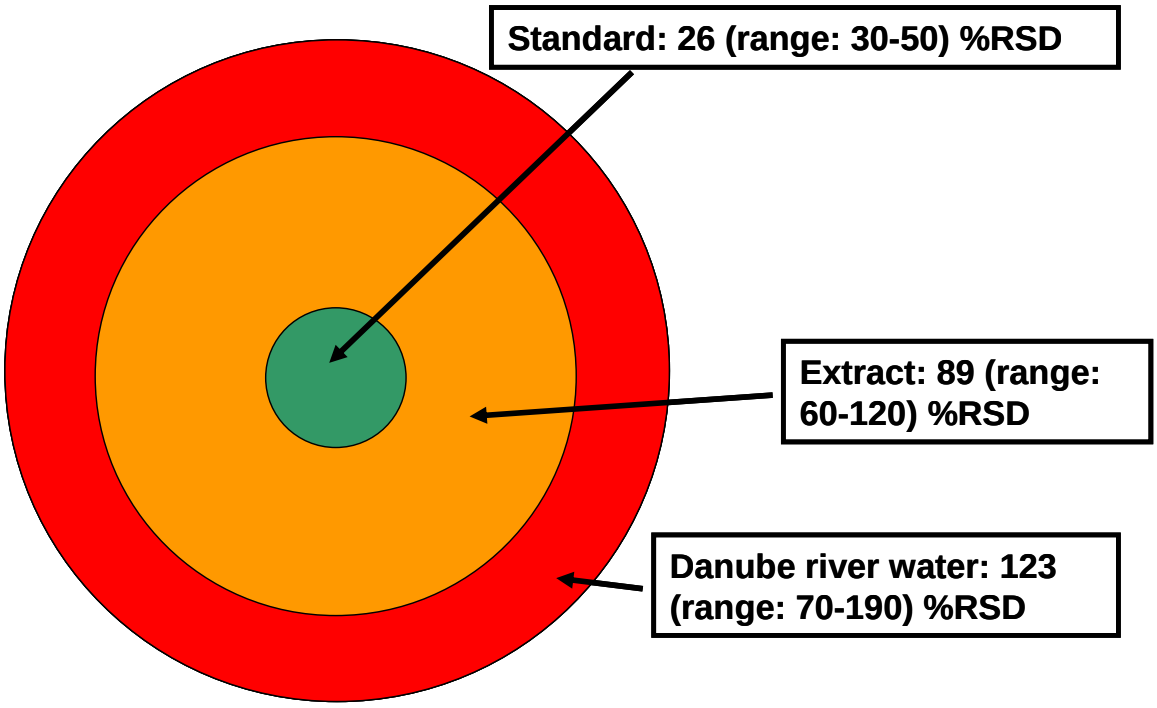


Figure 17: Variability of reported PBDE results in standard, homogenised extract and Danube river water. Results are average relative standard deviations for all PBDEs and in brackets the range for single PBDEs

In contrast to the observation for PAHs, the major contribution to the reported variability of results for PBDEs in Danube river water appears to result from sample treatment (clean-up etc.) prior to instrumental analysis in the laboratory. However, the concentrations of PBDEs in the homogenised extract were more than two orders of magnitude lower than in the standard solution. As a result only 7 of 16 laboratories reported values above their LOQ for the three most abundant BDE congeners 47, 99, and 100 in the extract compared to 15 of 16 laboratories for the standard solution. This suggests that the majority of the increased variability in the extract compared to the standard can be attributed to concentrations much closer to (or below) LOQ, where it is known that variability increases significantly, rather than to matrix challenges in the clean-up procedures. Also laboratory blanks, known to be an important issue for PBDEs (e.g., considered for method limits and detection limits in EPA Method 1614 on Brominated Diphenyl Ethers in Water Soil, Sediment and Tissue by HRGC/HRMS of August 2007) are likely to have caused more problems at 100 times lower concentrations in the extract compared to the standard. In the Danube river water average and median PBDE levels (sum of congeners 28, 47, 99, 100, 153, 154) were 0.32 ng/L and 0.16 ng/L, respectively, corresponding to 50% and 30% of EQS levels, respectively. Compared to the homogenised extract these concentrations are approximately 4000 times lower, which suggest that the extract and the river water have comparable levels for this exercise as a concentration of a 2-5 Liter water sample to 0.5- 1 ml in the final extract seems reasonable. Therefore, like for PAHs the sampling approach, sampling technique and sample storage till laboratory analyses still have a significant contribution to overall variability of Danube river water results for PBDEs. Similar to the observation for the homogenised extract only 6 out of 16 laboratories delivered results avove their LOQ for the three most abundant BDE congeners 47, 99, and 100, suggesting that it is possible to measure PBDEs in water at the levels

around (> 30%) the EQS, but only a few laboratories are yet ready for WFD monitoring (see also figures 18a and 18 b below).

6.2.5 Methods performance for PBDE WFD monitoring

Figure 18a: Number of laboratories that are ready (green) or not ready (red) for the sensitivity requirements of 30% EQS (30% of 0.5 ng/L sum of-BDE congener numbers 28, 47, 99, 100, 153 and 154 equals LOQ of 0.15ng/L for each single congener) as specified in the proposal for a Commission Directive on technical specifications for chemical analysis and monitoring of water status for PBDE WFD monitoring.

Of the 14 laboratories that reported LOQs only 6 have reported LOQs that comply with the 30% EQS requirements as foreseen in the proposal for a Commission Directive on technical specifications for chemical analysis and monitoring of water status (see figure 16a). However, as discussed for PAHs above, the EQS for PBDEs (0.5 ng/L) is set for the sum of BDE congener numbers 28, 47, 99, 100, 153 and 154 whereas each congener is analysed as single analyte having a single LOQ. Thus, an LOQ of 30% of that EQS would denote 0.15 ng/L for each analyte and a sum of these 6 LOQs 1 ng/L being 2 times the EQS. For avoiding this problem for WFD compliance checking the LOQ could be proposed as 1/6*30% EQS for each congener so that the sum of 6 times 0.025 ng/L results in 0.15 ng/L being 30% EQS. For this case only 3 out of the 14 laboratories reporting LOQs in this exercise would be ready for WFD monitoring (figure 16b).

Figure 18b: Number of laboratories that are ready (green) or not ready (red) for the sensitivity requirements of 30% EQS (1/6*30% of 0.5 ng/L sum of-BDE congener numbers 28, 47, 99, 100, 153 and 154 equals LOQ of 0.025 ng/L for each single congener) as specified in the proposal for a Commission Directive on technical specifications for chemical analysis and monitoring of water status for PBDE WFD monitoring.

This appears to be a more realistic picture of the actual situation evidenced also by the small number of laboratories delivering concentrations above LOQs in Danube river water in this exercise. It is important to note that only the three laboratories (out of the participating 16 for PBDE analyses in this exercise) applying high resolution mass spectrometric analysis in their methodology were ready for analysing at LOQs of 1/6*30% EQS (0.025 ng/L). In this context it is interesting to note that "method limits" (equal to LOQ) for analysis of Brominated Diphenyl Ethers in water by HRGC/HRMS in EPA Method 1614 are 0.1 ng/L for congener numbers 47 and 99 and 0.05 ng/L for congener numbers 28, 100, 153 and 154, respectively, for a 1L water sample. The sum of these LOQs would be 0.3 ng/L corresponding to 60% EQS, however, this method was not developed for WFD monitoring purposes and could probably be adapted easily to WFD requirements (e.g., by taking 2-5 L water samples). Nevertheless, it remains unclear whether high resolution mass spectrometry is the only way to comply with sensitivity needs or whether other methodologies (e.g., based on GC-MS-MS or GC-NCI-MS) could be also adapted for WFD monitoring.

6.3 Alkylphenol results from participating laboratories

For NP/OP fourteen laboratories reported analytical results.

6.3.1 Standard S3 and extract E2

For the NP/OP standard solution S3 reported results were in relatively good agreement .

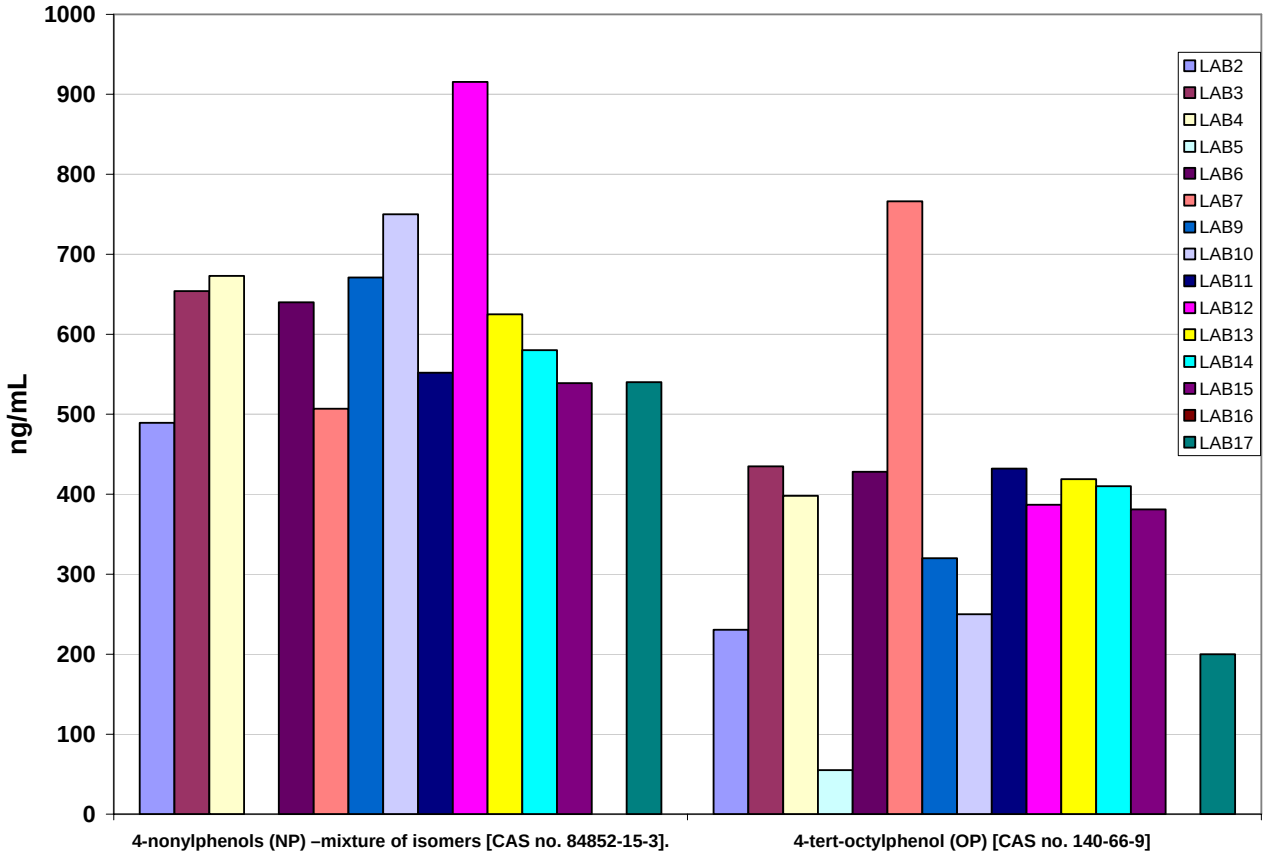


Figure 19: NP/OP in the standard S3

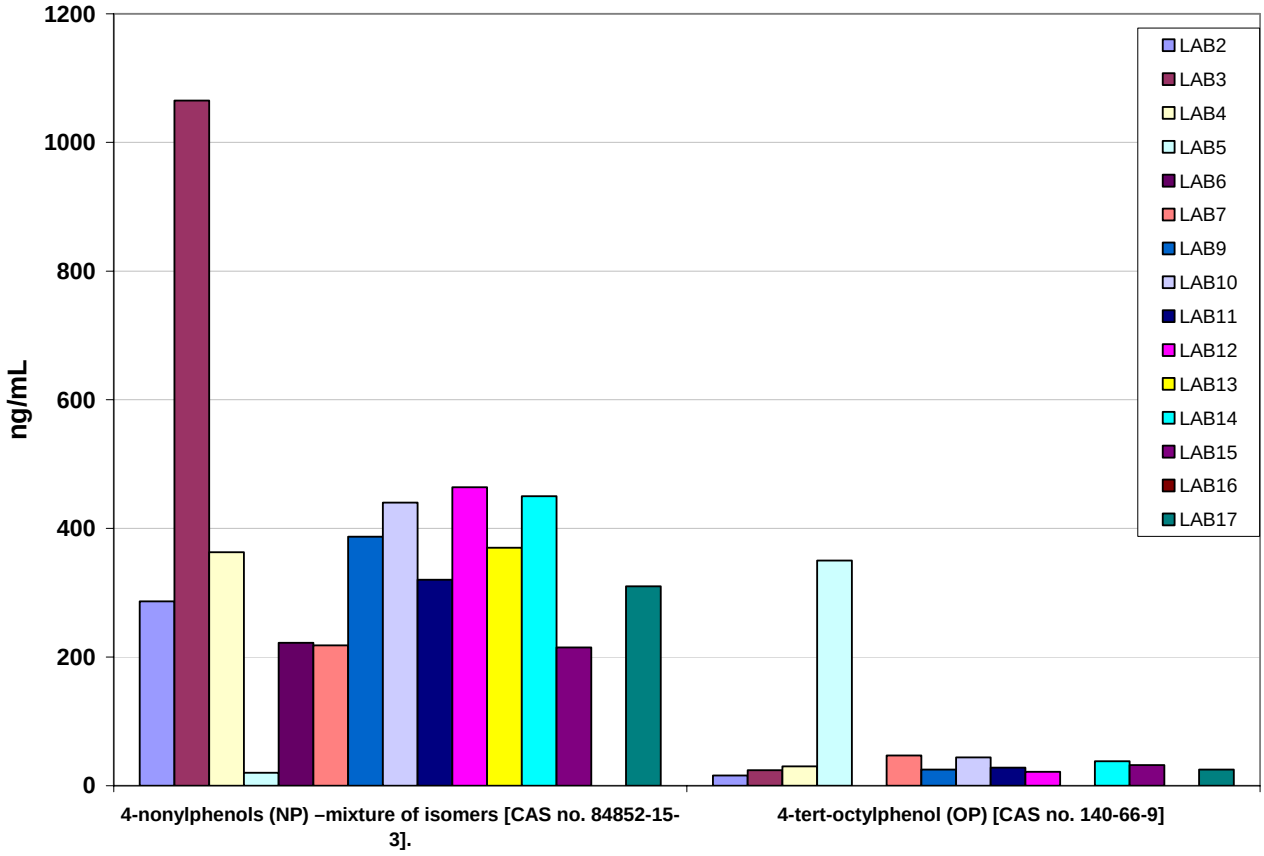


Figure 20: NP/OP in the river water extract E3

6.3.2 Danube River water

The analysis of NP/OP in the River Danube was difficult due to the low concentration levels. Figure 21 shows thus an inhomogeneous picture with only 3 results being reported for Octylphenol.

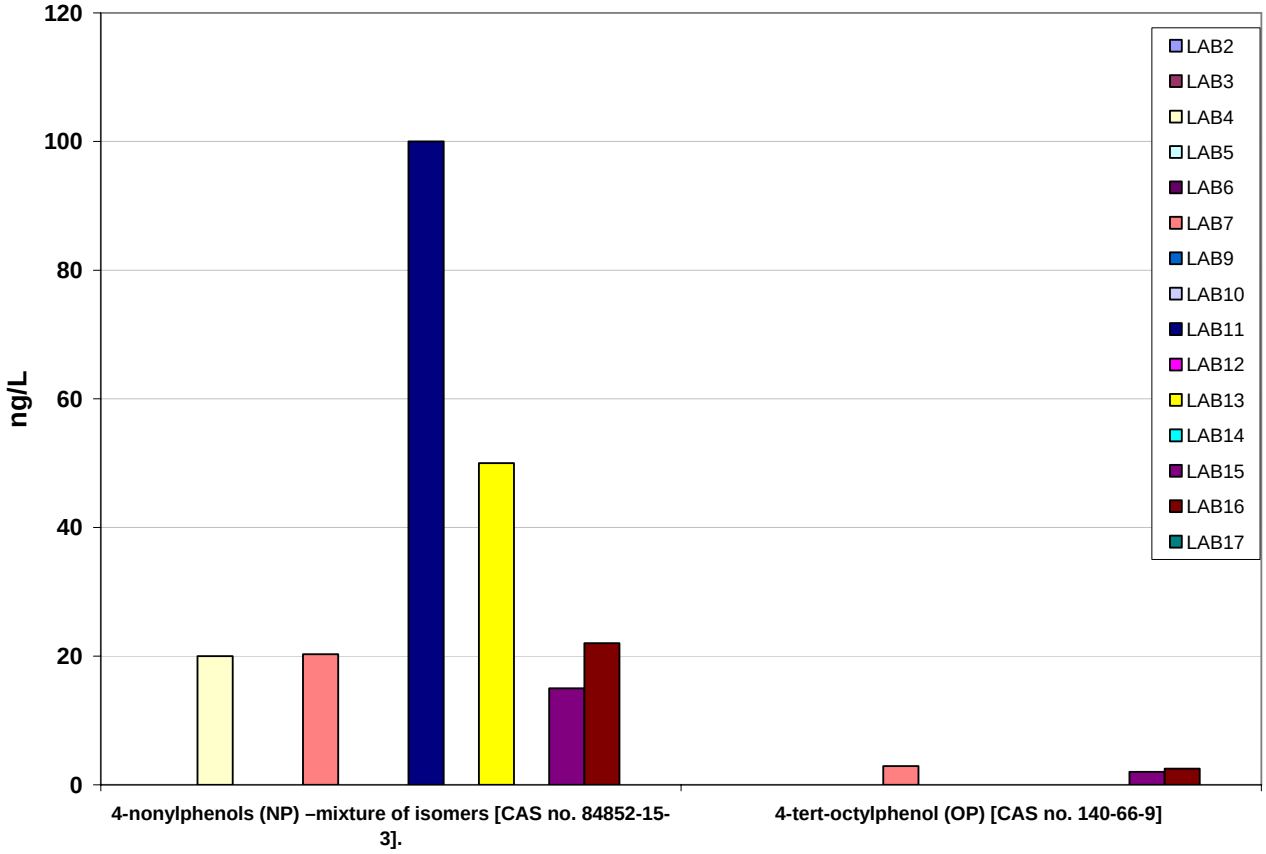


Figure 21 NP/OP in Danube River water

6.3.3 Variability in Nonylphenol / Octylphenol results

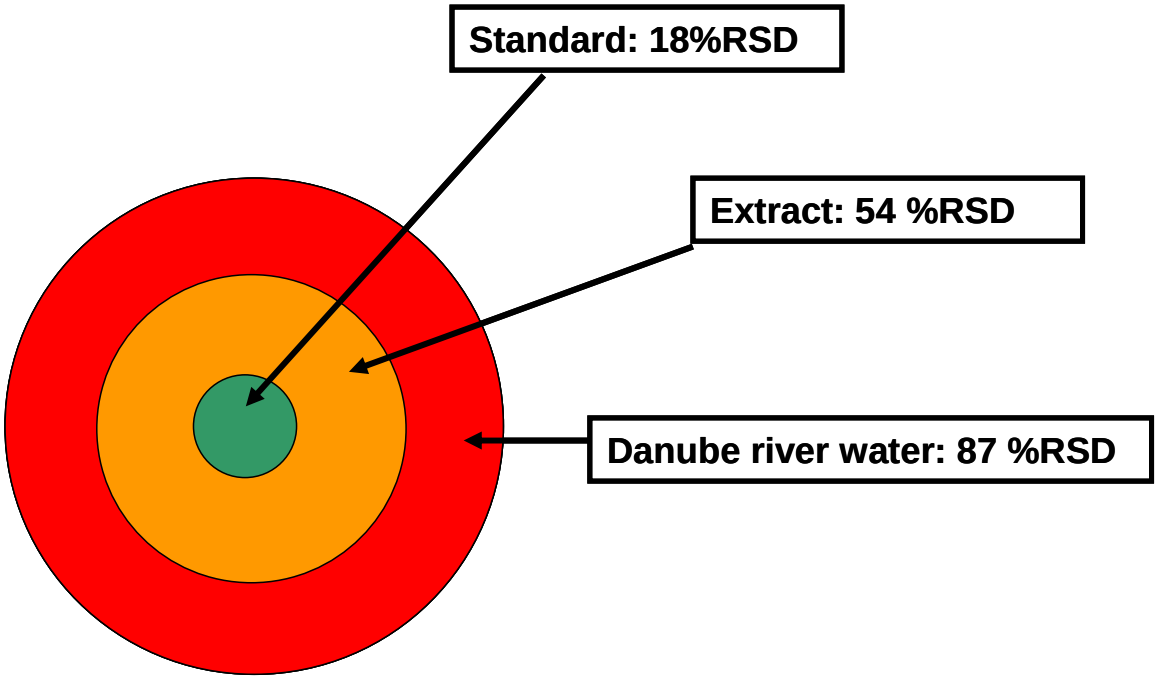


Figure 22a: Variability of reported Nonylphenol results in standard, homogenised extract and Danube river water. Results are given as relative standard deviations.

For Nonylphenol the observed variability of 87% in reported Danube river water results appears to be equally caused by the differences in the sampling approach, sampling technique and sample storage till laboratory analyses on the one hand and by matrix effects or clean-up procedures in sample preparation and instrumental analysis on the other side. Nonylphenol concentrations in the extract were about half of the concentrations in the standard solution so the observed differences in variability may be mainly attributed to analytical difficulties, such as ion suppression or interferences from nonylphenol ethoxylates in instrumental analyses (LC-MS) and sample preparation (clean-up, concentration procedures), respectively. In contrast, nonylphenol concentrations in the Danube river water were approximately 10% of Nonylphenol EQS (300 ng/L) and a factor of 10,000 lower than in the extract, which is probably 10 times more than the concentration factor in most applied procedures in this exercise. As a result only 6 out of 14 laboratories reporting data for Nonylphenol were able to report Danube river concentrations above their LOQ, or more precisely 4 laboratories reported concentrations at LOQ and 2 above their LOQs. Therefore, the main factor for the observed higher variability in Danube river water compared to the homogenised extract may well be that concentrations were around laboratories' LOQs, where increased variability is common.

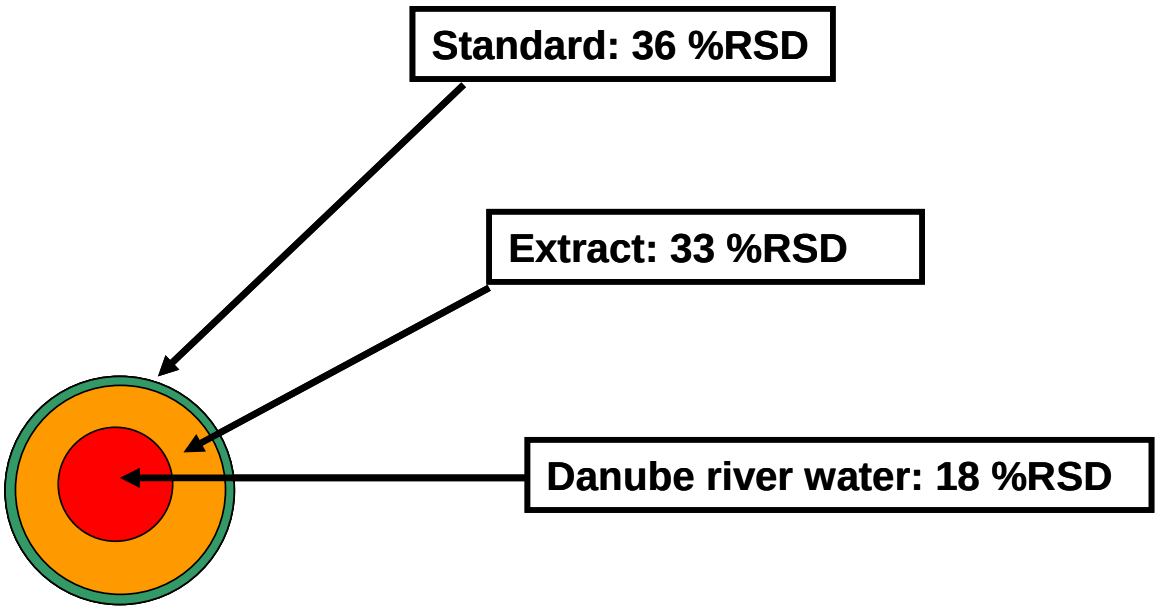


Figure 22b: Variability of reported Octylphenol results in standard, homogenised extract and Danube river water. Results are given as relative standard deviations.

The observed variabilities for reported results of octylphenol between standard solution, homogenised extract and Danube river water are surprising as for octylphenol (figure 22b) it suggests that Danube river water can be analysed with a lower variability than a standard solution. For understanding this apparent contradiction it should be noted that only 3 out of 14 laboratories reporting data for octylphenol have delivered results above their detection limit (in fact only two of them as the third laboratory reported results 10 times lower than the reported LOQ making the results questionable), but those 3 results were in good agreement. Nevertheless, it is not good practise to draw statistical conclusions from only 2 or 3 results and probably more important is the observation that Danube river octylphenol concentrations were below detection limits of most laboratories but also at least 50 times below the octylphenol EQS. So for octylphenol the observation remains that octylphenol results varied in both the standard solution and the homogenised extract (although a factor of 20 times lower concentrated than the standard solution) comparably and that matrix effects and concentration differences did not result in an increase of variability in the results for the extract in this exercise.

6.3.4 Methods performance for Nonylphenol / Octylphenol WFD monitoring

Figure 23: Number of laboratories that are ready (green) or not ready (red) for the sensitivity requirements of 30% EQS as specified in the proposal for a Commission Directive on technical specifications for chemical analysis and monitoring of water status for WFD chemical monitoring.

For nonylphenol / octylphenol only 4 out of 13 laboratories (only 2 for octhylphenol) that participated to this exercise have reported LOQs that did not reach the 30% EQS requirements as foreseen in the proposal for a Commission Directive on technical specifications for chemical analysis and monitoring of water status. Moreover, the 4 laboratories not complying with the sensitivity requirements of the Commission Directive have LOQs only little higher than required (mostly only by a factor of 2 or less) so that it can be assumed that little modifications in the analytical procedures or in sample volume would make those methods 'ready" as well. This indicates that many laboratories are nowadays prepared for monitoring nonylphenol and octylphenol for the WFD.

7 Conclusions

It was shown that even some of the most challenging WFD priority substances, selected on purpose for this exercise, can be measured at WFD relevant concentrations (> 0.3 x EQS) with methods currently applied in Member States. Depending on the analyte group, the obtained results were not within proposed data quality limits for some participants and therefore further development of methods and harmonisations of efforts is suggested.

Overall conclusions

- Environmental concentrations of PAH, PBDE and NP/OP can be analysed in surface waters at concentrations taking into account the set European Environmental Quality Standards values and the proposed performance criteria.
- Among the included analyte groups, PBDE appear to be the major challenge for monitoring at sub-ng/L level in water samples.
- Very much differing sampling and analytical methodologies are still in use within Member States
- Not all among the participating laboratories were able to deliver results at the required concentration levels
- No proficiency testing scheme or other external quality control possibility, taking into account the problematics of real environmental samples is available at present for these analyses
- In vicinity to the proposed EQS concentration levels high data quality is of importance for compliance checking
- Blank values in analytical procedures are of crucial importance, as analytical problems can lead also to an overestimation of pollutant content and consequently even to non-compliance
- The occurring variability of contaminants in surface waters is of utmost importance for the selection of the monitoring strategies and needs therefore to be studied

8 Outlook

Further joint on-site trials are being planned in the frame of the Chemical Monitoring Activity working group. It will be important that the exercises are reflecting the needs of Member States and help to harmonise approaches and their further development on European scale. While harmonisation of analytical methods is a key issue, also the further development of monitoring strategies, in particular the issues of sampling strategy and methodology is of importance.
While analytical methodology is under further development within CEN, it will be important to analyse the causes for current shortcomings and to agree on a common way forward within the Common Implementation Strategy for the Water Framework Directive in order to arrive at scientifically sound and harmonised chemical monitoring in Europe. These activities should be coordinated at European level by Member States experts.

The CMA On-site 2 participants and organising team

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10 References

European Commission, Circa homepage, 2009, http://circa.europa.eu/Public/irc/env/wfd/-home

Needs for reliable analytical methods for monitoring chemical pollutants in surface water under the EuropeanWater Framework Directive
Peter Lepom, Bruce Brown, Georg Hanke, Robert Loos, Philippe Quevauviller, JanWollgast,
Journal of Chromatography A, 1216 (2009) 302–315

CMA on-site 1 Final report: Comparison of Monitoring Approaches for Selected Priority Pollutants in Surface Water, EUR 22922 EN – 2007).
http://ies.jrc.ec.europa.eu/uploads/fileadmin/Documentation/Reports/RWER/EUR_2006-2007/EUR_22922.pdf

FRAMEWORK DIRECTIVE (2000/60/EC), Guidance Document No. 7, Monitoring under the Water Framework Directive, Luxembourg: Office for Official Publications of the European Communities, 2003, ISBN 92-894-5127-0, ISSN 1725-1087

European Commission, COMMON IMPLEMENTATION STRATEGY FOR THE WATER FRAMEWORK DIRECTIVE (2000/60/EC), Guidance Document No. 15, Guidance on Groundwater Monitoring, Luxembourg: Office for Official Publications of the European Communities, 2007, ISBN 92-79-04558-X, ISSN 1725-1087

European Commission, DIRECTIVE 2008/105/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council

European Commission, COMMON IMPLEMENTATION STRATEGY FOR THE WATER FRAMEWORK DIRECTIVE (2000/60/EC) Guidance Document No. 19 GUIDANCE ON SURFACE WATER CHEMICAL MONITORING UNDER THE WATER FRAMEWORK DIRECTIVE. 2009
http://circa.europa.eu/Public/irc/env/wfd/library?l=/framework_directive/guidance_documents/guidance_monitoringpdf/_EN_1.0_&a=d

DRAFT COMMISSION DIRECTIVE laying down, pursuant to Directive 2000/60/EC of the European Parliament and of the Council, technical specifications for chemical analysis and monitoring of water status, CMTD(2008)0130.

European Commission, 2000. Off. J. Europ. Commun., L 327, 22 Dec. 2000, DIRECTIVE 2000/60/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 23 October 2000 establishing a framework for Community action in the field of water policy.

European Commission, 2001, Off. J. Europ. Commun., L 327, 22 Dec. 2000, DECISION No. 2455/2001/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 20 November 2001 establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC.

European Commission, 2006, Off. J. European Union, L 372/19, DIRECTIVE 2006/118/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 12 December 2006 on the protection of groundwater against pollution and deterioration.

EPA, US Environmental Protection Agency, Method 1614, Brominated Diphenyl Ethers in Water, Soil, Sediment, and Tissue by HRGC/HRMS, August 2007, EPA-821-R-07-005

Annex I

Method information from all CMA-onsite 2 participants

Table 11: PAH Method Information

Laboratory code	LAB1	LAB1	LAB2
Danube River Water	**Danube River Water**	**Danube River Water**	**Danube River Water**
Volume [L]	2.3	29.1	9
Sampling method	SS-bucket	KNF-Pump (Teflon heads), Teflon tubing, GF/F 293 mm Filter and online XAD-2 extraction of PAHs	Pumping
Bottle type	brown glass bottle (cleaned solvent bottles)		Glass bottle
Bottle preparation	No		No
Sample transport + storage	Cooled	Cooled (XAD), frozen (GF/F)	Cooled
Sample pretreatment	No	no	No pretretment
SPM Extraction technique:			
Water Extraction technique:	LLE CH2Cl2		LLE CH2Cl2
			at neutral pH
Clean Up:	none	none	none
GC column:	DB-5ms	DB-5ms	Supelcosil LC18-PAH
Length	60m	60m	150*4,6 mm ; 5 µm
Film thickness	0.25µm	0.25µm	elution gradient :
Temperature program			water/acetonitrile
GC/MS system:	Agilent GC 6890N, Agilent MSD 5973	Agilent GC 6890N, Agilent MSD 5973	
Ionisation	EI	EI	
^{13}C/Deuterated Internal Standards	Anthracene, Fluoranthene, Benzo(a)pyrene, Benzo(b)fluoranthene, Indeno(1,2,3-cd)pyrene, Benzo(g,h,i)perylene	Anthracene, Fluoranthene, Benzo(a)pyrene, Benzo(b)fluoranthene, Indeno(1,2,3-cd)pyrene, Benzo(g,h,i)perylene	
^{13}C/Deuterated Recovery Standards	Pyrene, Benzo(e)pyrene, Benzo(k)fluoranthene	Pyrene, Benzo(e)pyrene, Benzo(k)fluoranthene	
Method:			ISO 17993
Measurement uncertainty(if available)			
Blank values			0
Comments:			analysed in LC/UV/Fluo method

(*): Specified filter type and cut size
(**): Specified adsorbent and/or solvent used

Table 11: PAH Method Information

Laboratory code	LAB3	LAB4	LAB4	LAB5	LAB6
Danube River Water	**Danube River Water**	**Danube River Water**	**Danube River Water**	**Danube River Water**	**Danube River Water**
Volume [L]	1	1 l	1 l	1	4L
Sampling method	direct bottle sampling			ss bucket	bottle sampling
Bottle type	Glass bottle with Teflon-lined screw cap, wrapped with aluminum foil	Glas Bottle	Glas Bottle	glass bottle	bottle PE
Bottle preparation					3 pre-rising with danube water
Sample transport + storage	cooled	4°C	4°C	cooled	cooled
Sample pretreatment	none				
SPM Extraction technique:					
Water Extraction technique:	SPDE (C18 disk 47mm diameter)			LLE	LLE
Clean Up:					
GC column:		UltraSep ES PAH	UltraSep ES PAH	DB-5	
Length		250 cm	250 cm	60m	
Film thickness		C18	C18	0.25	
Temperature program		Acetonitril/Wasser (50%/50%) in 40min auf 100% Acetonitril, 15 min 100% Acetonitril	Acetonitril/Wasser (50%/50%) in 40min auf 100% Acetonitril, 15 min 100% Acetonitril		
GC/MS system:				GC-MS/MS	
Ionisation				EI	
^{13}C/Deuterated Internal Standards				3	
^{13}C/Deuterated Recovery Standards	Fluoronaphtalene, Fluorophenanthrene, Fluoropyrene as surrogate standards			3	
Method:	EPA 8310 (HPLC-FLD)	DIN EN ISO 17993	DIN EN ISO 17993		
Measurement uncertainty(if available)					
Blank values					
Comments:					HPLC-FLUO / method : NF EN ISO 17993

(*): Specified filter type and cut size
(**): Specified adsorbent and/or solvent used

Table 11: PAH Method Information

Laboratory code	LAB7	LAB8	LAB9
Danube River Water	**Danube River Water**	**Danube River Water**	**Danube River Water**
Volume [L]	1	2.5	1
Sampling method	Direct bottle sampling	direct bottle sampling,..	bucket (plastic)
Bottle type	Amber glass solvent bottle	Solvent bottle: 2,5 L	amber glass bottle
Bottle preparation	Solvent cleaning, pre-rinsing	Solvent cleaning	
Sample transport + storage	Cooled	cooled	styrofoam box, cooled
Sample pretreatment		Filtration:Millipore, filter type HA, pore size 0,45 µm	
SPM Extraction technique:		ASE: 70/30 acetone/n-hexane v/v	
Water Extraction technique:	LLE	SPE: isolute PAH, C18	LLE, n-hexane
Clean Up:		Silica column	
GC column:	DB-5	DB 17ms	ZB-5
Length	60m	30 m	30 m
Film thickness	0.25µm	0,25 µm	0,25 µm
Temperature program	70ºC 1min, 20ºC/min, 180ºC 1min, 5ºC/min, 310ºC 15min; Injection T. 270ºC	T_0 = 60°C for 1 min **Rate (°C/min) / T_{fin} (°C) / final time (min)** 30 / 130 / 1 8 / 190 / 5 6 / 310 / 27	50 °C ->300 °C
GC/MS system:	MD-800, Low Resolution MS (SIM)	LRGC/LRMS Agilent Technologies 5975 Inert	Agilent GC 6890N, Agilent MSD 5973
Ionisation	EI (70eV)	EI	EI
^{13}C/Deuterated Internal Standards	3, added before the extraction	2: Chrysene-d12, Indeno (1,2,3-cd)-d12 pyrene added before the injection in GC/MS	
^{13}C/Deuterated Recovery Standards	1, added to the final extract just before the analysis by GC/MS	5: Fenanthrene-d10, Fluoranthene-d10, Benzo(a)anthracene-d12, Benzo(a)pyrene-d12, Dibenzo(a,h)anthracene-d14, Dibenzo(a,i)pyrene-d14 added before the extraction 3 Antracene d10, Benzo(b)fluorantene d12, Benzo(g,h,i)perilene d12 added just after the sampling and before the sample pretreatment (filtration)	
Method:	EPA 1625	EPA 3545A, EPA3630C, EPA8270D	ISO/DIS 28540
Measurement uncertainty(if available)		Measurement uncertainty in progress, we have given uncertainty calculated with the Horwitz function	
Blank values	Fluoranthene: 0.7ng/L	The blank values have been substracted to SPM values	0
Comments:	LRMS SIM Method: 14 ions monitored in 2 functions (dwell time 70-90ms)		

(*): Specified filter type and cut size
(**): Specified adsorbent and/or solvent used

Table 11: PAH Method Information

Laboratory code	LAB10		LAB11
Danube River Water	**Danube River Water**	**Danube SPM**	**Danube River Water**
Volume [L]	1	1810	10 liter
Sampling method	bucket	centrifuge	bucket
Bottle type	Glass Bottle		glass bottle
Bottle preparation			solveny cleaning (cyclohex)
Sample transport + storage	Ambient temperature (transport, appr. 12 h) + cooled (storage)		transport:ambient temp.; storage:4°C
Sample pretreatment	unfiltered		extraction in sampling bottle
SPM Extraction technique:		1 g dry material, ultrasonic extraction with acetone	
Water Extraction technique:	LLE with cyclohexane		LLE, continuous extraction, 24u cyclohex.
Clean Up:	sodium sulfate		no clean up
GC column:	DB-5		Vydac 201TP
Length	30 m		25 cm x 4.6 mm; 5µ
Film thickness	0.25 µm		
Temperature program	70 °C (1 min), 8 °C/min to 130 °C, 6 °C/min to 300 °C (4 min)		
GC/MS system:	PerkinElmer Turbomass Q-MS		Agilent 1100
Ionisation	EI		FLU-DET
^{13}C/Deuterated Internal Standards	7		
^{13}C/Deuterated Recovery Standards			methyl chtyseen
Method:			Home method
Measurement uncertainty(if available)			
Blank values			< LOD
Comments:			

(*): Specified filter type and cut size
(**): Specified adsorbent and/or solvent used

Table 11: PAH Method Information

Laboratory code	LAB12	LAB13
Danube River Water	**Danube River Water**	**Danube River Water**
Volume [L]	1 L	0.57
Sampling method	direct bottle sampling using a "bottle on a pole" system	stainless steel bucket
Bottle type	1L Amber glass bottles with a wide mouth	brown glass bottles (for solvents)
Bottle preparation	Glassware washing using a professional wash machine, drying at 180°C for 3h, rinsing with a small volume of HPLC grade methanol. Bottles were rinsed with river water before sampling	solvent cleaning (methanol or acetone)
Sample transport + storage	cooled	extraction on site
Sample pretreatment	no filtration	no filtration; 0.5% methanol added to sample before extraction
SPM Extraction technique:		
Water Extraction technique:	LLE LLE with n-hexane; A conical flask with a ground joint neck is filled with 1 L sample of water. 5 g NaCl and 5 mL of 50% H_2SO_4 are added. The extraction is performed with 10 mL n-hexane on a magnetic stirrer using a PTFE-coated stir bar. During extraction, the flask is closed using a PTFE stopper. Extraction time is 2 hours. Following extraction, the organic phase extract is separated using a glass column microseparator containing 0.5 g of anhydrous sodium sulphate. A defined portion of the extract is transferred using a Pasteur pipette to a conical test tube. The solvent is removed using a gentle stream of nitrogen at room temperature. The analytes are redissolved in 200 ul acetonitrile and the extract is transferred to a conical autosampler vial. 15 ul of the extracts are injected to HPLC.	SPE SUPELCO C18 1g conditioning: 5 mL dichloromethane, 10 mL methanol; 20 mL ultrapure water. Drying time: 30-40 min. Elution: 20 mL CH_2Cl_2, reduced to 200 µL mL under nitrogen stream and reconstituted to 0.5 mL with ACN:H_2O 60:40 (v/v)
Clean Up:	no	
GC column: Length Film thickness Temperature program GC/MS system: Ionisation	HPLC system Agilent HP 1100, HPLC column SUPELCOSIL LC-PAH 57945 2.1 mm x 25 cm, particle diameter 5um gradient elution; mobile phase A: acetonitrile; B: 5% acetonitrile in water fluorescence detector Agilent HP 1200 Various substance specific combinations of excitation/emission wavelenghts	 Supelco LC-PAH 4.6x250 mm water, acetonitrile;gradient: 25min linear gradient from initial water:ACN ratio 40.60 v/v to a final ratio 0:100 v/v, followed by a 15 min isocratic step at 0:100 v/v and by a 5 min decreasing linear gradient to 40:60 v/v
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards		Fluorescence λ_{ex}=250, λ_{em}= 460 from 0 to 18 min; λ_{ex}= 290, λ_{em}=418 from 18 to 28 min; λ_{ex}= 290, λ_{em}=490 from 28 min to the end of chromatogram
Method: Measurement uncertainty(if available) Blank values		internal method Benzo(k)fluoranthene: 0.4 ng/L
Comments:		

(*): Specified filter type and cut size
(**): Specified adsorbent and/or solvent used

Table 11: PAH Method Information

Laboratory code	LAB14	LAB15	LAB16	LAB17
Danube River Water	**Danube River Water**	**Danube River Water**	**Danube River Water**	**Danube River Water**
Volume [L]	4L	1	1	1 l
Sampling method		bucket	bucket (metal)	Bucket, stainlss steel
Bottle type	Glass bottles	glass	glass bottle	Glasbottle
Bottle preparation	Solvent cleaning, prerinsing	solvent cleaning	pre-rinsing	pre-rinsing
Sample transport + storage	Cooled	ambient/cooled	cooled	cooled
Sample pretreatment	Filtration	no	-	no pretreatment
SPM Extraction technique:	Sohxlet extraction	no	-	
Water Extraction technique:	LLE	LLE	lle	LLE, hexane
Clean Up:	Silica column	silica	SiO2	no clean up
GC column:	Chromspher PAH, 5um C18 packed	Rtx dioxin2	Rtx-5Sil MS	Restek RTx-5Sil MS
Length		40	30m	30m x 0,25mm
Film thickness	Acetonitrile/water 50:50 gradient to 100% Acetonitrile	0.18	0.25µm	0,25µm
Temperature program	1 ml/min 28 C		oven: 50C(1m), 30C/m, 140C (0m), 10C/m, 320C (8m), injector: 50C(0.6m), 999C/min, 250C	90°(1min) --40°/min--> 165° --4°/min--> 205° --5°/min--> 305° --25°/min--> 325°(3.8min)
GC/MS system:	HPLC-Fluorescence, 363 Varian , Prostar 240 Varian	Agilent 5973i	Perkin Elmer LR-MS AutosystemXL/Turbomass	Agilent GC/MSD 5975
Ionisation		EI	EI+	EI
^{13}C/Deuterated Internal Standards	2,2- binaftyl		DPAH (3)	16 ^{13}C-PAHs according to EPA-PAHs, added to extract
^{13}C/Deuterated Recovery Standards	1647e	5		
Method:		MSZ 1484-6	EPA 8270D	according to DIN 38407 F39
Measurement uncertainty(if available)	17%		-	
Blank values			0	
Comments:			-	

(*): Specified filter type and cut size
(**): Specified adsorbent and/or solvent used

Table 11: PAH Method Information

Laboratory code	LAB18	LAB19	LAB20
Danube River Water	**Danube River Water**	**Danube River Water**	**Danube River Water**
Volume [L]	2,5 L	2	2
Sampling method	taking water with bucket and poor the bottle.	pumping	direct bottle sampling
Bottle type	Dark Solvent bottle	glass bottle	Glass Bottle
Bottle preparation	Solvent cleaning and pre-rinsing	heating, pre-rinsing	Solvent cleaning
Sample transport + storage	On 4 C in refrigerator	cooled	Cooled
Sample pretreatment	no	-	no
SPM Extraction technique:	no	-	
Water Extraction technique:	LLE	LLE (n-hexane)	LLE
Clean Up:	no	Silica column	Silica column
GC column:	HP-5 MSI J&W Scientific	Rtx-XLB	HP-5 MS
Length	30 m	30m	30 m
Film thickness	0.25µm	0.5µm	0,25 um
Temperature program	40C for 1min; 40-100C at 15C/min; 100-240C at 20C/min; 240-300C at 10C/min,for 3 min	40°C 3min, 20°C/min, 180°C 10min, 10°C/min, 330°C 14min	60 C (2 min), 8 C/min 290 C, 4 C/min 300 C (8 min)
GC/MS system:	Agilent 6890N/5975MSD Low Res / Inlet Mode: Pulsed Splitless Injection	Perkin-Elmer AutoSystem XL Perkin-Elmer TurboMass	Low Res GC/MS
Ionisation	EI	EI	EI
^{13}C/Deuterated Internal Standards	Acenaphthene-D10, Phenanthrene-D10,	2	5
^{13}C/Deuterated Recovery Standards	Fluoranthene-D10	4	5
Method:	EPA 8270	MSZ 1484-6:2003	MSZ 1484-6:2003
Measurement uncertainty(if available)			
Blank values	Reagent Water Blank	-	
Comments:		-	

(*): Specified filter type and cut size
(**): Specified adsorbent and/or solvent used

Table 11: PAH Method Information

Laboratory code	LAB21	LAB22
Danube River Water	**Danube River Water**	**Danube River Water**
Volume [L]	1	6
Sampling method		
Bottle type	glass bottle	
Bottle preparation		
Sample transport + storage	cooled in 4 °C	4 ºC
Sample pretreatment		
SPM Extraction technique:		
Water Extraction technique:	LLE with dichloromethane	LLE
Clean Up:	silica column	Silica column
GC column:	DB-5	RTX-5SIL MS
Length	30 m	30
Film thickness	0,25 µm	0.1
Temperature program	45 °C(1 min) 8 °C/min, 300 °C	50ºC 1 min,15ºC/min to 130ºC,8ºC/min to 280 ºC
GC/MS system:	Low Res	HP6890/5973 GC-MS
Ionisation	EI	EI
^{13}C/Deuterated Internal Standards		1
^{13}C/Deuterated Recovery Standards	used 6	5
Method:	MSZ 1484-6:2003	MSZ 1484-6:1998
Measurement uncertainty(if available)	± 10 %	
Blank values		<1 ng/ml
Comments:		

(*): Specified filter type and cut size
(**): Specified adsorbent and/or solvent used

Table 11: PAH Method Information

Laboratory code	LAB1	LAB1	LAB2
Extract E1	**Extract E1**	**Extract E1**	**Extract E1**
Clean Up:	if different	if different	if different
GC column: Length Film thickness Temperature program GC/MS system: Ionisation			
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards			
Method: Measurement uncertainty(if available) Blank values			
  Comments:			

Laboratory code	LAB1	LAB1	LAB2
	Standard S2	**Standard S2**	**Standard S2**
GC column: Length Film thickness Temperature program GC/MS system: Ionisation	if different	if different	if different
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards			
Method: Measurement uncertainty(if available) Blank values			
  Comments:			

Table 11: PAH Method Information

Laboratory code	LAB3	LAB4	LAB4	LAB5	LAB6
Extract E1	**Extract E1**	**Extract E1**	**Extract E1**	**Extract E1**	**Extract E1**
Clean Up:	if different	if different	if different	if different	if different
GC column: Length Film thickness Temperature program GC/MS system: Ionisation					
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards					
Method: Measurement uncertainty(if available) Blank values					
  Comments:					 HPLC-FLUO / method : NF EN ISO 17993

Laboratory code	LAB3	LAB4	LAB4	LAB5	LAB6
	Standard S2	**Standard S2**	**Standard S2**	**Standard S2**	**Standard S2**
GC column: Length Film thickness Temperature program GC/MS system: Ionisation	if different	if different	if different	if different	if different
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards					
Method: Measurement uncertainty(if available) Blank values					
  Comments:					 HPLC-FLUO / method : NF EN ISO 17993

Table 11: PAH Method Information

Laboratory code	LAB7	LAB8	LAB9
Extract E1	**Extract E1**	**Extract E1**	**Extract E1**
Clean Up:		no	if different
GC column: Length Film thickness	DB-5 60m 0.25µm	DB 17ms 30 m 0,25 µm T_0 = 60°C for 1 min Rate (°C/min) T_{fin} (°C) final time (min) 30 130 1 8 190 5 6 310 27	
Temperature program	70ºC 1min, 20ºC/min, 180ºC 1min, 5ºC/min, 310ºC 15min; Injection T. 270ºC		
GC/MS system:	Low Resolution (SIM)	LRGC/LRMS Agilent Technologies 5975 Inert	
Ionisation	EI (70eV)	EI	
^{13}C/Deuterated Internal Standards	3, added before the analysis by GC/MS	2: Chrysened12, Indeno (1,2,3-cd)-d12 pyrene added before the injection in GC/MS 5: Fenanthrene-d10, Fluoranthene-d10, Benzo(a)anthracene-d12, Benzo(a)pyrene-d12, Dibenzo(a,h)anthracene-d14, Dibenzo(a,i)pyrene-d14 added before the injection	
^{13}C/Deuterated Recovery Standards			
Method: Measurement uncertainty(if available) Blank values	EPA 1625	EPA8270D uncertainty measurement in progress, we have given uncertainty calculated with Horwitz function	0
Comments:	LRMS SIM Method: 14 ions monitored in 2 functions (dwell time 70-90ms)		

Laboratory code	LAB7	LAB8	LAB9
	Standard S2	**Standard S2**	**Standard S2**
GC column: Length Film thickness	DB-5 60m 0.25µm	DB 17ms 30 m 0,25 µm T_0 = 60°C for 1 min Rate (°C/min) T_{fin} (°C) final time (min) 30 130 1 8 190 5 6 310 27	if different
Temperature program	70ºC 1min, 20ºC/min, 180ºC 1min, 5ºC/min, 310ºC 15min; Injection T. 270ºC		
GC/MS system:	Low Resolution (SIM)	LRGC/LRMS Agilent Technologies 5975 Inert	
Ionisation	EI (70eV)	EI	
^{13}C/Deuterated Internal Standards	3, added before the analysis by GC/MS	2: Chrysene-d12, Indeno (1,2,3-cd)-d12 pyrene added before the injection in GC/MS 5: Fenanthrene-d10, Fluoranthene-d10, Benzo(a)anthracene-d12, Benzo(a)pyrene-d12, Dibenzo(a,h)anthracene-d14, Dibenzo(a,i)pyrene-d14 added before the injection	
^{13}C/Deuterated Recovery Standards			
Method: Measurement uncertainty(if available) Blank values	EPA 1625	EPA8270D uncertainty measurement in progress, we have given uncertainty calculated with Horwitz function no	0
Comments:	LRMS SIM Method: 14 ions monitored in 2 functions (dwell time 70-90ms)		

Table 11: PAH Method Information

Laboratory code	LAB10		LAB11
Extract E1	**Extract E1**		**Extract E1**
Clean Up:	if different		no clean up ***Solvent not compatible for HPLC***
GC column: Length Film thickness Temperature program GC/MS system: Ionisation			HT-5 12m 0.1 µm 60(3)-50-260(0)-30-300°C(12) Polaris -Q ion trap EI
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards			external stand.: on column inj.
Method: Measurement uncertainty(if available) Blank values			Home method < LOQ
Comments:			***GCMS is not a routine VMM-method for PAH***

Laboratory code	LAB10		LAB11
	Standard S2		**Standard S2**
GC column: Length Film thickness Temperature program GC/MS system: Ionisation	if different		if different
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards			
Method: Measurement uncertainty(if available) Blank values			
Comments:			***GCMS is not a routine VMM-method for PAH***

Table 11: PAH Method Information

Laboratory code	LAB12	LAB13
Extract E1	**Extract E1**	**Extract E1**
Clean Up:	no cleanup	if different
GC column: Length Film thickness Temperature program GC/MS system: Ionisation	HPLC system Agilent HP 1100, HPLC column SUPELCOSIL LC-PAH 57945 2.1 mm x 25 cm, particle diameter 5um gradient elution; mobile phase A: acetonitrile; B: 5% acetonitrile in water fluorescence detector Agilent HP 1200 Various substance specific combinations of excitation/emission wavelenghts	
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards		
Method: Measurement uncertainty(if available) Blank values		
Comments:	The extract was evaporated to dryness with nitrogen and redissolved in acetonitrile for HPLC analysis. Conditions of HPLC analysis were identical to those used for the Danube River water sample extract. External calibration standard was used for quantification.	

Laboratory code	LAB12	LAB13
		Standard S2
GC column: Length Film thickness Temperature program GC/MS system: Ionisation	 **Standard S2** HPLC system Agilent HP 1100, HPLC column SUPELCOSIL LC-PAH 57945 2.1 mm x 25 cm, particle diameter 5um gradient elution; mobile phase A: acetonitrile; B: 5% acetonitrile in water	if different
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards	fluorescence detector Agilent HP 1200 Various substance specific combinations of excitation/emission wavelenghts	
Method: Measurement uncertainty(if available) Blank values		
Comments:	Because of the incompatibility of n-nonane with the HPLC mobile phase the extract was evaporated using a gentle stream of nitrogen to dryness and redissolved in the same volume of acetonitrile. For HPLC analysis, undiluted sample was injected (15 ul) Conditions of HPLC analysis were identical to those used for the Danube River water sample extract. External calibration standard was used for quantification.	

Table 11: PAH Method Information

Laboratory code	LAB14	LAB15	LAB16	LAB17
Extract E1	**Extract E1**	**Extract E1**	**Extract E1**	**Extract E1**
Clean Up:	if different	if different	if different	if different
GC column: Length Film thickness Temperature program GC/MS system: Ionisation				
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards				
Method: Measurement uncertainty(if available) Blank values				
  Comments:				

Laboratory code	LAB14	LAB15	LAB16	LAB17
	Standard S2	**Standard S2**	**Standard S2**	**Standard S2**
GC column: Length Film thickness Temperature program GC/MS system: Ionisation	if different	if different	if different	if different
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards				
Method: Measurement uncertainty(if available) Blank values				
  Comments:				

Table 11: PAH Method Information

Laboratory code	LAB18	LAB19	LAB20
Extract E1	**Extract E1**	**Extract E1**	**Extract E1**
Clean Up:	if different	-	if different
GC column: Length Film thickness		Rtx-XLB 30m 0.5μm	HP-5 MS 30 m 0,25 um
Temperature program		40°C 3min, 20°C/min, 180°C 10min, 10°C/min, 330°C 14min	60 C (2 min), 8 C/min 290 C, 4 C/min 300 C (8 min)
GC/MS system: Ionisation		Perkin-Elmer AutoSystem XL Perkin-Elmer TurboMass EI	Low Res GC/MS EI
^{13}C/Deuterated Internal Standards		2	5
^{13}C/Deuterated Recovery Standards		4	5
Method: Measurement uncertainty(if available) Blank values		MSZ 1484-6:2003 -	MSZ 1484-6:2003
Comments:		-	

Laboratory code	LAB18	LAB19	LAB20
	Standard S2	**Standard S2**	**Standard S2**
GC column: Length Film thickness	if different	if different	see Extract E1
Temperature program			
GC/MS system: Ionisation		Perkin-Elmer AutoSystem XL Perkin-Elmer TurboMass EI	
^{13}C/Deuterated Internal Standards		2	
^{13}C/Deuterated Recovery Standards		4	
Method: Measurement uncertainty(if available) Blank values		MSZ 1484-6:2003 -	
Comments:		-	

Table 11: PAH Method Information

Laboratory code	LAB21	LAB22
Extract E1	**Extract E1**	**Extract E1**
Clean Up:	if different	if different
GC column: Length Film thickness Temperature program GC/MS system: Ionisation		
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards		
Method: Measurement uncertainty(if available) Blank values		
  Comments:		

Laboratory code	LAB21	LAB22
	Standard S2	**Standard S2**
GC column: Length Film thickness Temperature program GC/MS system: Ionisation	if different	if different
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards		
Method: Measurement uncertainty(if available) Blank values		
   Comments:		

Table 12: PBDE Method Information

Laboratory code	LAB1	LAB2	LAB3
Danube River Water	**Danube River Water**	**Danube River Water**	**Danube River Water**
Sampling start (for all samples)			
Sampling end (for all samples)			
Sample Volume [L]			1
Sampling method			direct bottle sampling
Bottle type			Glass bottle with Teflon-lined screw cap, wrapped with aluminum foil
Bottle preparation			
Sample transport + storage			cooled
Sample pretreatment			none
SPM Extraction technique:			
Water Extraction technique:			stir bar sorptive extraction (SBSE); twister retroextracted with acetonitrile (100µl) and with isopropyl alcohol (100µl)
Clean Up:			none
GC column:	BP SOL-GEL1ms		Stx-500
Length	15M		15 m
Film thickness	0.1		0.15 µm
Temperature program			100°C for 1,40 min; 60°C/min to 180°C; 30°C/min to 320°C; 320°C for 8 min
Volume injected	1µl		25 µl, PTV, solvent vent mode
GC/MS system:	HRGC-HRMS		Agilent 5973, Low Res, single quad
Ionisation	EI AT 37eV		EI
^{13}C/Deuterated Internal Standards			13C: BDE28, BDE47, BDE99, BDE153, BDE138
^{13}C/Deuterated Recovery Standards	8		
Others (F,Br-BDE,…….)			
Standard Method:	EPA1614		ISO 22032
Measurement uncertainty(if available)			
Blank values			lower than 0.2 ng/l for all PBDEs
Comments:			

(*): Specified filter type and cut-off size
(**): Specified adsorbent and/or solvent used

Table 12: PBDE Method Information

Laboratory code	LAB4	LAB5	LAB6
Danube River Water	**Danube River Water**	**Danube River Water**	**Danube River Water**
Sampling start (for all samples)	18/09/08 11:00	12:00	18/09/08 -11h00
Sampling end (for all samples)	18/09/08 11:15	12:10	18/09/08 -11h15
Sample Volume [L]	1	1	4
Sampling method	direct bottle sampling	ss bucket	bottle sampling
Bottle type	glass bottle	glass bottle, green	bottle PE
Bottle preparation		none	3 pre-rinsing with danube water
Sample transport + storage	cooled 4°C	cooled	cooled
Sample pretreatment			
SPM Extraction technique:		These results from outsourced laboratory.	
Water Extraction technique:	LLE		LLE, CH2Cl2
	Toluen 50ml		
Clean Up:			no
GC column:	DB-5MS		DB5-MS
Length	15m		25m
Film thickness	0,1µm		0.25µm
Temperature program	80°C 0,5min; 12°C/s 280°C 2min; 1°C/min 340°C 10min		40°C to 230°C at 20°C/min-230 to 285°C at 6°C/min-285 to 340°C at 25°C/min-340°C for 5min
Volume injected	2µl		30µl
GC/MS system:	GC/DSQ		Quadripole-low res
			Mode SIM
Ionisation	NCI		NCI
^{13}C/Deuterated Internal Standards			1
^{13}C/Deuterated Recovery Standards			
Others (F,Br-BDE,…….)			2
Standard Method:			ISO22032
Measurement uncertainty(if available)			
Blank values			<0.25 ng/L
Comments:		These results from outsourced laboratory.	no

(*): Specified filter type and cut-off size
(**): Specified adsorbent and/or solvent used

Table 12: PBDE Method Information

Laboratory code	LAB7	LAB9	LAB10
Danube River Water	**Danube River Water**	**Danube River Water**	**Danube River Water**
Sampling start (for all samples)		10:50	18/09/08 11:45
Sampling end (for all samples)		10:55	18/09/08 12:00
Sample Volume [L]	1	4	1.921
Sampling method	Direct bottle sampling	bucket (plastic)	bucket
Bottle type	Amber glass solvent bottle	amber glass bottle	Glass Bottle
Bottle preparation	Solvent cleaning, pre-rinsing		
Sample transport + storage	Cooled	styrofoam box, cooled	Ambient temperature + cooled
Sample pretreatment			
SPM Extraction technique:			
Water Extraction technique:	LLE, CH2Cl2	LLE, n-hexane	LLE Toluene
Clean Up:			SiOH/H2SO4
GC column:	DB-5MS	ZB-5	RTX CLP
Length	10m	30 m	30 m
Film thickness	0.18µm	0,25 µm	0.25µm
Temperature program	140ºC 1min, 15ºC/min, 250ºC 1min, 10ºC/min, 310ºC 5 min; Injection T. 280ºC	100 °C -> 300 °C	
Volume injected	1µL	1 µl	
GC/MS system:	AutoSpec Ultima, High Resolution MS	Agilent GC 7890A, Agilent MSD 5975C	GC/MSD
Ionisation	EI (30eV)	EI	NCI
^{13}C/Deuterated Internal Standards	8, added before the extraction		F-BDE 28,100,208
^{13}C/Deuterated Recovery Standards	3, added to the final extract just before the analysis by GC/MS		FF-BDE 47, 201
Others (F,Br-BDE,…….)			13C BDE 209
Standard Method:	EPA 1614	ISO/DIS 22032	
Measurement uncertainty(if available)			
Blank values	BDE-47: 0.03ng/L; BDE-100: 0.01ng/L	0	BDE47: 0.002 ng/L; BDE209: 0.005 ng/L
Comments:	HRMS SIM Method: 38 ions monitored in 6 functions (dwell time 50ms)		All results BDE congeners are blank corrected

(*): Specified filter type and cut-off size
(**): Specified adsorbent and/or solvent used

Table 12: PBDE Method Information

Laboratory code	LAB10		LAB11
Danube River Water	**Danube SPM**	**whole SPM sample dry material**	**Danube River Water**
Sampling start (for all samples)			in group
Sampling end (for all samples)			in group
Sample Volume [L]	1810	25.38 g	10
Sampling method	centrifuge		bucket
Bottle type			glass bottle
Bottle preparation			solvent cleaning (cyclohex)
Sample transport + storage			transport:ambient temp.; storage:4°C
Sample pretreatment			extraction in sampling bottle
SPM Extraction technique:	5.0045 g dry material, ASE Toluene		
Water Extraction technique:			LLE, continuous extraction, 24u cyclohex.
Clean Up:	GPC SiOH/H2SO4		GPC clean up Envirogel™
GC column: Length Film thickness			5MS 15m 0.1 µm
Temperature program			80(2)-15-230(2)-5-270(0)-10-330(0)
Volume injected			1 µl PTV
GC/MS system:			High Res; DFS
Ionisation			EI
^{13}C/Deuterated Internal Standards			PBDE 77, PBDE 181, PBDE 209-$^{13}C_{12}$
^{13}C/Deuterated Recovery Standards			Dibromooctafluorobiphenyl (DBOFBP)
Others (F,Br-BDE,…….)			
Standard Method:			Home method
Measurement uncertainty(if available)			validation ongoing
Blank values			<LOD
Comments:			

(*): Specified filter type and cut-off size
(**): Specified adsorbent and/or solvent used

Table 12: PBDE Method Information

Laboratory code	LAB12	LAB13	LAB14
Danube River Water	**Danube River Water**	**Danube River Water**	**Danube River Water**
Sampling start (for all samples)	18.9.2008, according to agreed schedule		
Sampling end (for all samples)	18.9.2008, according to agreed schedule		
Sample Volume [L]	1	5.5	5
Sampling method	direct bottle sampling using a "bottle on a pole" system	Stainless Bucket	
Bottle type	1L Amber glass bottles with a wide mouth	Glass	Glass bottles
Bottle preparation	Glassware washing using a professional wash machine, drying at 180°C for 3h, rinsing with a small volume of HPLC grade methanol. Bottles were rinsed with river water before sampling	Solvent cleaning and silanization with chlorosilanes	Solvent cleaning, prerinsing
Sample transport + storage	Cooled at 4°C	Transport and storage at 4 °C	Cooled
Sample pretreatment	no filtration	Fitration on 0.7 µm glass fiber filter	Filtration
SPM Extraction technique:	not performed	Automated Soxhlet, acetone/*n*-hexane 1:3 v/v	Sohxlet
Water Extraction technique:	Stir bar sorptive extraction (SBSE) To the water sample (100 mL) in a 250 mL glass bottle 20 mL of methanol and 10 µL of BDE-77 internal standard solution (0.05 µg/mL) was added to give a concentration of 5.0 ng/L. The sample was extracted using stir bar sorptive extraction (SBSE) for 60 min at 600 rpm. After extraction, stir bar (Twister from Gerstel) was removed from the sample, dried and placed in the liner of a TDU thermal desorption system (Gerstel, Mühlheim a.d. Ruhr, Germany).	SPE C18 (BakerBond Speedisk) Elution with *n*-hexane/ethylacetate 9:1 v/v	LLE pentane/ether
Clean Up:	none	Silica gel/H_2SO_4 30% w/w, 2 g Elution with *n*-hexane/Dichloromethane 1:1 v/v, 10 mL concentration under nitrogen stream; extract final volume 100 µL	Aluminumoxide, acid treatment
GC column:	HP-5MS column (Agilent Technologies) 30 m × 250 µm I.D., 0.25 µm df	Restek Rtx-5MS	CP-SIL 8 CB
Length	30 m	60 m x 0.25 mm	50
Film thickness	0.25µm….	0.25 µm	0.25um
Temperature program	80 ºC (1 min) at 30 ºC/min to 200 ºC and at 5 ºC/min to 285 ºC Solvent venting thermal desorption of Twister stir bar was performed by programming TDU from 40 to 280 ºC (6 min) at a rate of 12 ºC/s. The analytes were focused in the glass wool packed liner of the PTV at 20 ºC prior to injection. For splitless injection (2 min) the PTV was ramped from 20 ºC to 280 ºC at a rate of 12 ºC/s.	Injection by Programmable Temperature Vaporizer injector; GC run: Initial temp 60 °C X 2 min, then 40 ºC/min to 230 ºC (held 0.1 min), then 3 ºC to 280 ºC (held 25 min); He 1.1 ml/min, transfer line 280 ºC; MS souce 250 ºC	
Volume injected		2 µL	0.8
GC/MS system:	Agilent 6890 GC + Agilent 5973 low resolution MSD; Agilent Technologies, Palo Alto, CA, USA. The system was equipped with a TDU and a CIS4 programmed temperature vaporisation (PTV) injector system (Gerstel, Mühlheim/Ruhr, Germany).	Thermo Electron Trace GC/PolarisQ Ion Trap Mass Spectrometer	Varian 3800
Ionisation	EI The MSD was used in the selected ion monitoring (SIM) mode, targeting three ions for each PBDE	EI in MS/MS mode	
^{13}C/Deuterated Internal Standards		[$^{13}C_{12}$]BDE-77, 126	
^{13}C/Deuterated Recovery Standards		[$^{13}C_{12}$]BDE-28, 47, 99 153, 154, 183	
Others (F,Br-BDE,…….)	BDE 77		BDE-119, octachloronaphtalene
Standard Method:	no		
Measurement uncertainty(if available)	not available		
Blank values		Below LOQs	
Comments:	To the water sample (100 mL) in a 250 mL glass bottle 20 mL of methanol and 10 µL of BDE-77 internal standard solution (0.05 µg/mL) was added to give a concentration of 5.0 ng/L. The sample was extracted using stir bar sorptive extraction (SBSE) for 60 min at 600 rpm. After extraction, stir bar (Twister from Gerstel) was removed from the sample, dried and placed in the liner of a TDU thermal desorption system (Gerstel, Mühlheim a.d. Ruhr, Germany). The GC-MS analysis was performed using Agilent 6890 gas chromatograph coupled to Agilent 5973 mass spectrometric detector (MSD; Agilent Technologies, Palo Alto, CA, USA). The system was equipped with a TDU and a CIS4 programmed temperature vaporisation (PTV) injector system (Gerstel). Solvent venting thermal desorption was performed by programming TDU from 40 to 280 ºC (6 min) at a rate of 12 ºC/s. The analytes were focused in the glass wool packed liner of the PTV at 20 ºC prior to injection. For splitless injection (2 min) the PTV was ramped from 20 ºC to 280 ºC at a rate of 12 ºC/s. Capillary GC analysis was performed on a 30 m × 250 µm I.D		

(*): Specified filter type and cut-off size
(**): Specified adsorbent and/or solvent used

Table 12: PBDE Method Information

Laboratory code	LAB15	LAB16	LAB17
Danube River Water	**Danube River Water**	**Danube River Water**	**Danube River Water**
Sampling start (for all samples)		18.9.08 at 11am (?)	
Sampling end (for all samples)		18.9.08 (?+15min)	
Sample Volume [L]	1	1	1
Sampling method	bucket	bucket (metal)	bucket, stainlss steel
Bottle type	glass	glass bottle	glasbottle
Bottle preparation	solvent cleaning	pre-rinsing	pre-rinsing
Sample transport + storage	cooled	cooled	cooled
Sample pretreatment		-	no pretreatment
SPM Extraction technique:		-	
Water Extraction technique:	LLE, n-pentane	LLE, CH2Cl2	LLE, hexane
Clean Up:	AgNO3/acid/base	SiO2 column	no clean up
GC column:	Rtx dioxin2	Rtx-5Sil MS	Restek RTx-5Sil MS
Length	40	30m	30m x 0,25mm
Film thickness	0.18	0.25µm	0,25µm
Temperature program		oven: 100C(1m), 10C/m, 320C (7m), injector: 50C(0.6m), 999C/min, 300C	150°(1min) --30°/min--> 200° --5°/min--> 290°(14.3min)
Volume injected	2	5µl	5µl
GC/MS system:	Agilent 5973i	Perkin Elmer LR-MS AutosystemXL/Turbomass	Agilent GC/MSD 5975
Ionisation	EI	EI+	EI
^{13}C/Deuterated Internal Standards		-	^{13}C-BDE 100 + ^{13}C-BDE 153, added to solvent used for LLE
^{13}C/Deuterated Recovery Standards		-	
Others (F,Br-BDE,…….)	PCB209; 4,4-dibromo-biphenyl	decachlorobiphenyl	
Standard Method:	EPA1614	EPA 8270D	
Measurement uncertainty(if available)		-	
Blank values		0	
Comments:		-	

(*): Specified filter type and cut-off size
(**): Specified adsorbent and/or solvent used

Table 12: PBDE Method Information

Laboratory code	LAB1	LAB2	LAB3
Extract E1	**Extract E1**	**Extract E1**	**Extract E1**
Clean Up:	NONE		
GC column: Length Film thickness Temperature program Volume injected	if different	if different	if different
GC/MS system:			
Ionisation			
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards Others (F,Br-BDE,…….)			
Standard Method: Measurement uncertainty(if available)			
Blank values			lower than 0.2 ng/ml for all PBDEs
Comments:			

Laboratory code	LAB1	LAB2	LAB3
Standard S1	**Standard S1**	**Standard S1**	**Standard S1**
GC column: Length Film thickness Temperature program Volume injected	if different	if different	if different
GC/MS system:			
Ionisation			
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards Others (F,Br-BDE,…….)			
Standard Method: Measurement uncertainty(if available)			
Blank values			lower than 0.2 ng/ml for all PBDEs
Comments:			

Table 12: PBDE Method Information

Laboratory code	LAB4	LAB5	LAB6
Extract E1	**Extract E1**	**Extract E1**	**Extract E1**
Clean Up:		none	no clean-up
GC column: Length Film thickness Temperature program Volume injected	if different	DB-1MS 30m 0.25 35-320 1 µl	if different
GC/MS system:		Agilent low res MS	
Ionisation		NCI	
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards Others (F,Br-BDE,…….)			
Standard Method: Measurement uncertainty(if available)			
Blank values		0	
Comments:		concentration based on external calibration	

Laboratory code	LAB4	LAB5	LAB6
Standard S1	**Standard S1**	**Standard S1**	**Standard S1**
GC column: Length Film thickness Temperature program Volume injected	if different	as extract	if different
GC/MS system:			
Ionisation			
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards Others (F,Br-BDE,…….)			
Standard Method: Measurement uncertainty(if available)			
Blank values			
Comments:		concentration based on external calibration	

Table 12: PBDE Method Information

Laboratory code	LAB7	LAB9	LAB10
Extract E1	**Extract E1**	**Extract E1**	
Clean Up:			**Extract E1** GPC SiOH/H2SO4
GC column: Length Film thickness Temperature program Volume injected	DB-5MS 10m 0.18µm 140ºC 1min, 15ºC/min, 250ºC 1min, 10ºC/min, 310ºC 5 min; Injection T. 280ºC 1µL	if different	
GC/MS system:	AutoSpec Ultima, High Resolution MS		
Ionisation	EI (30eV)		
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards Others (F,Br-BDE,…….)	8, added before the analysis by GC/MS		
Standard Method: Measurement uncertainty(if available)	EPA 1614		
Blank values		0	
Comments:	HRMS SIM Method: 38 ions monitored in 6 functions (dwell time 50ms)		

Laboratory code	LAB7	LAB9	LAB10
Standard S1	**Standard S1**	**Standard S1**	**Standard S1**
GC column: Length Film thickness Temperature program Volume injected	DB-5MS 10m 0.18µm 140ºC 1min, 15ºC/min, 250ºC 1min, 10ºC/min, 310ºC 5 min; Injection T. 280ºC 1µL	if different	
GC/MS system:	AutoSpec Ultima, High Resolution MS		
Ionisation	EI (30eV)		
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards Others (F,Br-BDE,…….)	8, added before the analysis by GC/MS		
Standard Method: Measurement uncertainty(if available)	EPA 1614		
Blank values		0	
Comments:	HRMS SIM Method: 38 ions monitored in 6 functions (dwell time 50ms)		

Table 12: PBDE Method Information

Laboratory code	LAB10		LAB11
Extract E1			**Extract E1**
Clean Up:			no clean up
GC column: Length Film thickness Temperature program Volume injected			if different
GC/MS system:			
Ionisation			
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards Others (F,Br-BDE,…….)			
Standard Method: Measurement uncertainty(if available)			
Blank values			
Comments:			

Laboratory code	LAB10		LAB11
Standard S1			**Standard S1**
GC column: Length Film thickness Temperature program Volume injected			if different
GC/MS system:			
Ionisation			
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards Others (F,Br-BDE,…….)			
Standard Method: Measurement uncertainty(if available)			
Blank values			
Comments:			

Table 12: PBDE Method Information

Laboratory code	LAB12	LAB13	LAB14
Extract E1	**Extract E1**	**Extract E1**	**Extract E1**
Clean Up:	no		Aluminumoxide column
GC column: Length Film thickness Temperature program Volume injected	HP-5MS column (Agilent Technologies) 30 m × 250 µm I.D., 0.25 µm df 30 m 0.25µm…. 80 ºC (1 min) at 30 ºC/min to 200 ºC and at 5 ºC/min to 285 ºC 30μL + 1uL internal standard solution (BDE 77, 0.5 ug/ml in hexane) was applied to the glass liner for thermal desorption and the solvent was allowed to evaporate	if different	if different
GC/MS system:	Agilent 6890 GC + Agilent 5973 low resolution MSD; Agilent Technologies, Palo Alto, CA, USA. The system was equipped with a TDU and a CIS4 programmed temperature vaporisation (PTV) injector system (Gerstel, Mühlheim/Ruhr, Germany).		
Ionisation	EI The MSD was used in the selected ion monitoring (SIM) mode, targeting three ions for each PBDE		
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards Others (F,Br-BDE,…….)	 BDE 77		
Standard Method: Measurement uncertainty(if available)	no		
Blank values			
Comments:			

Laboratory code	LAB12	LAB13	LAB14
Standard S1	**Standard S1**	**Standard S1**	**Standard S1**
GC column: Length Film thickness Temperature program Volume injected	HP-5MS column (Agilent Technologies) 30 m × 250 µm I.D., 0.25 µm df 30 m 0.25µm…. 80 ºC (1 min) at 30 ºC/min to 200 ºC and at 5 ºC/min to 285 ºC 10μL + 1uL internal standard solution (BDE 77, 0.5 ug/ml in hexane) was applied to the glass liner for thermal desorption and the solvent was allowed to evaporate	if different	if different
GC/MS system:	Agilent 6890 GC + Agilent 5973 low resolution MSD; Agilent Technologies, Palo Alto, CA, USA. The system was equipped with a TDU and a CIS4 programmed temperature vaporisation (PTV) injector system (Gerstel, Mühlheim/Ruhr, Germany).		
Ionisation	EI The MSD was used in the selected ion monitoring (SIM) mode, targeting three ions for each PBDE		
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards Others (F,Br-BDE,…….)	 BDE 77		
Standard Method: Measurement uncertainty(if available)	no		
Blank values			
Comments:		see report for Standard Deviation	

Table 12: PBDE Method Information

Laboratory code	LAB15	LAB16	LAB17
Extract E1	**Extract E1**	**Extract E1**	**Extract E1**
Clean Up:		if different	
GC column: Length Film thickness Temperature program Volume injected	if different		if different
GC/MS system:			
Ionisation			
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards Others (F,Br-BDE,…….)			
Standard Method: Measurement uncertainty(if available)			
Blank values			
Comments:			

Laboratory code	LAB15	LAB16	LAB17
Standard S1	**Standard S1**	**Standard S1**	**Standard S1**
GC column: Length Film thickness Temperature program Volume injected	if different	if different	if different
GC/MS system:			
Ionisation			
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards Others (F,Br-BDE,…….)			
Standard Method: Measurement uncertainty(if available)			
Blank values			
Comments:			

Table 13: Alkylphenol Method Information

Laboratory code	LAB2	LAB3
Danube River Water	**Danube River Water**	**Danube River Water**
Sample Volume [L]	1L	1
Sampling method	Pumping	direct bottle sampling
Bottle type	Glass Bottle	Glass bottle with Teflon-lined screw cap, wrapped with aluminum foil
Bottle preparation	No	Acid (HCl) rinsing, baking at 450˚C, solvent cleaning (acetone, n-hexane)
Sample transport	Cooled	cooled
Sample preservation	No	adding preservative (1 mL HCl 37%); refrigerating at 4˚C in the dark
Sample pretreatment and SPM separation	No pretreatment	none
Time between sampling and analysis	24h (sampling - extraction)	2 + 1/2 months
SPM Extraction technique:		
Water Extraction technique:	SPE	LLE
LLE		toluene (40 mL), manual mixing (1L glass funnel); dry extract on anhydrous sodium sulfate
SPE cartridge	chromabond easy	no
SPE conditions	pH3 / conditionning ether/methanolwater / Elution solvant :10mL ether/methanol 90/10	no
Clean Up:	-	1.5 g silica column (deactivated with milliQ water, 5% w/w); elution with toluene (45 mL)
SPE cartridge	chromabond easy	no
Derivatisation	BSTFA	none
GC column:	BPX35	DB-5 type (Restek Rxi-5ms)
Length	30m	25m
Film thickness	0,25µm	0.33µm
Temperature program	100°c 2min; 100 -> 310°C (10°C/min)	90˚C (1 min); 10 ˚C /min - 200 ˚C (0 min); 7 ˚C /min - 220 ˚C (0 min); 25 ˚C /min - 280˚C (2 min)
LC column:		
i.d. x lenght		
mobile phase		
Detector		
Wavelenghts		
GC/MS system:	MS-MS (ion trap)	HRGC - LRMS. GC: Thermo model TraceGC. MS: ion trap Thermo model PolarisQ; acquisition in Full Scan mode.
LC/MS system		
ions monitored	NP : 221-> 163+179+193 OP : 207->151+163+179	MS acquisition range: [50-400] m/z. **4-t-OP:**107,135 (quantification: 107+135); **4-NP**: 107, 121, 135 (quantification: 107)
LC/MS-MS transitions used		
Ionisation	EI	EI
ion suppression evaluated		
^{13}C/Deuterated Internal Standards	internal standard BPAd16 (before inejction)	^{13}C6 4-n-NP, added before LLE.
^{13}C/Deuterated Recovery Standards	surrogate 4nNPd8 (before extraction)	
Method:	-	ISO 18857-1:2005, modified
Measurement uncertainty(if available)		CV<25% (1L milliQ water with 3% NaCl,spiked with the analytes at concentrations 3xLOQ; 3 replicates)
Blank values	0,03 µg/L NP ; < LQ OP	<1/3 of LOQ; not subtracted (analysis of 1L milliQ water with 3% NaCl, 2 replicates)
Comments:		Stored at -20˚C in the dark until analysis

(*): Specified filter type and cut-off size
(**): Specified adsorbent and/or solvent used

Table 13: Alkylphenol Method Information

Laboratory code	LAB4	LAB4	LAB5	LAB6
Danube River Water	**Danube River Water**	**Danube River Water**	**Danube River Water**	**Danube River Water**
Sample Volume [L]	0.95		as PBDE and PAHs	4L
Sampling method				bottle sampling
Bottle type	Glass Bottle	Glass Bottle		bottle PE
Bottle preparation				3 pre-rising with danube water
Sample transport	4°C	4°C		cooled
Sample preservation				refrigerating
Sample pretreatment and SPM separation				
Time between sampling and analysis				7 days
SPM Extraction technique:				
Water Extraction technique:	LLE	SPE	LLE	LLE
LLE	n-Hexan, 40ml	Aceton	Hexane pH 13-14	sample acidifed at pH=2 and ELL by 40 ml of toluene during 4 hours
SPE cartridge		SDB; Baker		
SPE conditions		Aceton		
Clean Up:				no
SPE cartridge				no
Derivatisation			pentafluorobenzoylchloride	no
GC column:	RTX-5	DB-35MS	DB1-MS	DB5 ms
Length	30m	30m	30m	30m
Film thickness	0,25µm	0.25µm	0.25µm	0.25µm
Temperature program	100°C, 1min --> 10°C/min auf 200° --> 7°C/min auf 250°C, 10min	80°C 2min; 20°C/min 340°C 10min		100°C for 5min-10°C/min to 200°C-7°C/min to 250°C-250°C for 10min
LC column:				
i.d. x lenght				
mobile phase				
Detector				
Wavelenghts				
GC/MS system:	GC-MSD	GC-DSQ	Agilent GCMS	Ion trap - low resolution
LC/MS system				
ions monitored			400 / 414	107 and 135
LC/MS-MS transitions used				
Ionisation	EI	EI	NCI	EI
ion suppression evaluated				
^{13}C/Deuterated Internal Standards	4-n-Nonylphenol (Ring$^{13}C_6$)	**Mixture**[1]	2	1
^{13}C/Deuterated Recovery Standards				1
Method:	DIN EN ISO 18857-1	**DIN EN ISO 18857-2**		NF EN Iso 18857-1
Measurement uncertainty(if available)				
Blank values				CAS 84852-15-3: <50ng/L and CAS 140-66-9: <4ng/L
Comments:				

(*): Specified filter type and cut-off size
(**): Specified adsorbent and/or solvent used

Table 13: Alkylphenol Method Information

Laboratory code	LAB7	LAB9	LAB10		LAB11
Danube River Water	**Danube River Water**	**Danube River Water**	**Danube River Water**	**Danube SPM**	**Danube River Water**
Sample Volume [L]	1	1	1	1810	1 liter
Sampling method	Direct bottle sampling	bucket (plastic)		centrifuge	bucket
Bottle type	Amber glass solvent bottle	amber glass bottle	glass bottle		glass bottle
Bottle preparation	Solvent cleaning, pre-rinsing	pre-rinsing			solvent cleaning (n hex.)
Sample transport	Cooled	styrofoam box, cooled			transport:ambient temp.; storage:4°C
Sample preservation		cooling (4°C-8°C)	refrigerating		$CuSO_4$, pH<2 (H_2SO_4)
Sample pretreatment and SPM separation		pH=2			
Time between sampling and analysis	11 days	6 days			7 days for water sample; 1 month for std. and extr.
SPM Extraction technique:				1 g dry material, ultrasonic extraction with cyclohexane:acetone (9:1, v:v)	
Water Extraction technique:	LLE		SPE		LLE (= 80 ML)
LLE	2 extractions with 100mL of dichloromethane each one				n Hex. + derivatisation with pentafluorobenzoylchloride
SPE cartridge		Biotage ENV+ 200mg/6ml	StrataX (Phenomenex)		
SPE conditions		ethyl acetate	Acetone (2x2 mL)		
Clean Up:			none.		pré-extr. n hex. pH>11, derivatisation pH>8,<10
SPE cartridge		ethyl acetate, acetone			
Derivatisation		diazomethane	MSTFA + 0.6% TMIS		pentafluorobenzoylchloride
GC column:	DB-5	ZB-5	MDN-5 (Supelco)		BPX-35
Length	60m	30 m	30 m		50m
Film thickness	0.25µm	0,25 µm	0.25 µm		0.3µm
Temperature program	70ºC 1min, 20ºC/min, 180ºC 1min, 5ºC/min, 310ºC 15min; Injection T. 270ºC	60 °C -> 280 °C	70 °C (2 min), 16 °C/min to 180 °C, 5 °C/min to 290 °C (8 min)		PTV inj:65(1)-5-190(2)-2-230(2)-25-325(23)
LC column:					
i.d. x lenght					
mobile phase					
Detector					
Wavelenghts					
GC/MS system:	MD-800, Low Resolution MS (SIM)	Agilent GC 6890N, Agilent MSD 5973	Agilent Technologies (GC 6890, 5975 MSD)		Agilent low. Res. MSD; ECNI
LC/MS system					
ions monitored	113, 135, 157, 179, 188, 189, 206, 223, 228, 270, 314		NP: 179, OP: 207		m/z=414 (nonyl) ; 400 (octyl)
LC/MS-MS transitions used					
Ionisation	EI (70eV)	EI	EI		
ion suppression evaluated					
^{13}C/Deuterated Internal Standards	3, added before the extraction		none.		4-n-nonylphenol $^{13}C_6$; added before extr.
^{13}C/Deuterated Recovery Standards	1, added to the final extract just before the analysis by GC/MS		none.		-
Method:	EPA 1625	ISO/DIS 18857-2			Home method
Measurement uncertainty(if available)					
Blank values	NP: 11.9ng/L; OP: 2.3ng/L: NP_1EO: 5.4ng/L	0			< LOD
Comments:	LRMS SIM Method: 11 ions monitored in 1 functions (dwell time 50ms)				

(*): Specified filter type and cut-off size
(**): Specified adsorbent and/or solvent used

Table 13: Alkylphenol Method Information

Laboratory code	LAB12	LAB13	LAB14
Danube River Water	**Danube River Water**	**Danube River Water**	**Danube River Water**
Sample Volume [L]	1 L	3	2.0
Sampling method	direct bottle sampling using a "bottle on a pole" system	stainless steel bucket	direct bottle sampling
Bottle type	1L Amber glass bottles with a wide mouth	brown glass bottles (for solvents)	brown glass bottle
Bottle preparation	Glassware washing using a professional wash machine, drying at 180°C for 3h, rinsing with a small volume of HPLC grade methanol. Bottles were rinsed with river water before sampling	solvent cleaning (methanol or acetone)	heated 400°C
Sample transport	Cooled at 4°C	no	in insulated box
Sample preservation	refirgerating	no	acidified, refrigerated
Sample pretreatment and SPM separation	no filtration	Filtration with GF/F glass filter; 0.7 micron nominal pore size	glass fiber filter GF/C, suction
Time between sampling and analysis	sampling was performed on 18.9.2008 and sample extraction on 22.9.2008	on site filtration and extraction <1 month for analysis	4 weeks
SPM Extraction technique:	not	Randall extraction with hot methanol	solvent extraction of filter, sonication and shaker
Water Extraction technique:	LLE, 1 L of water	SPE	SPE
LLE	LLE with n-hexane; A conical flask with a ground joint neck is filled with 1 L sample of water. 5 g NaCl and 5 mL of 50% H2SO4 are added. The extraction is performed with 10 mL n-hexane on a magnetic stirrer using a PTFE-coated stir bar. During extraction, the flask is closed using a PTFE stopper. Extraction time is 2 hours. Following extraction, the organic phase extract is separated using a glass column microseparator containing 0.5 g of anhydrous sodium sulphate. A defined portion of the extract is transferred using a Pasteur pipette to a conical test tube. The solvent is removed using a gentle stream of nitrogen at room temperature. The analytes are redissolved in 200 ul acetonitrile and the extract is transferred to a conical autosampler vial. 15 ul of the extracts are injected to HPLC.		
SPE cartridge		Strata C18-Unendcapped (Phenomenex) 6 ml, 500 mg;	Isolute ENV+
SPE conditions		conditioning: 10 mL acetone, 10 mL methanol; 10 mL ultrapure water. Drying time: 30 min. Elution: 10 mL acetone reduced to 0.5 mL under nitrogen stream	cond: acetone, water elute: ecetonitrile, tetrahydrofurane, hexane+MTBE
Clean Up: SPE cartridge		For SPM: Silica column 9 g activated at 160°C	after acetylation: silica column, hexane
Derivatisation			acetylation
GC column: Length Film thickness			VF-5 MS, Varian 30m x 0,25 mm 0,25 µm
Temperature program			50 to 300 °C
LC column: i.d. x lenght	HPLC system Agilent HP 1100, HPLC column LiChrosphere 4 mm x 12.5 cm, particle diameter 5um	Luna Phenyl-Hexyl (Phenomenex) 5 micron, 4.6x250 mm Solvent water: methanol: 1 mL/min. Gradient: from 40:60 to 20:80 in 35 min, then to 100% methanol at 40 min	
mobile phase	gradient elution; mobile phase A: 50% acetonitrile in methanol; B: 5% acetonitrile in water		
Detector	fluorescence detector Agilent HP 1200	Fluorescence:	
Wavelenghts	Excitation/Emission = 232/310 nm	ex 230 nm; em 302 nm	
GC/MS system: LC/MS system			Agilent 6890N-5973N Low res
ions monitored			NP: 107, 135, 149 OP 135, 177
LC/MS-MS transitions used			
Ionisation			EI
ion suppression evaluated			
^{13}C/Deuterated Internal Standards	not used		
^{13}C/Deuterated Recovery Standards	not used		3-Etyl-4-chlorophenol, before SPE
Method:		Internal (proposed IRSA-APAT method)	
Measurement uncertainty(if available)			
Blank values		dissolved: all<LOD; SPM OP<LOD; NP<50 ng/l; NPE1< 50 ng/l; NPE2<15 ng/l	NP: 9, 15, 18 ng/l OP: 1.0, 1.6. 1.6 ng/l
Comments:			

(*): Specified filter type and cut-off size
(**): Specified adsorbent and/or solvent used

Table 13: Alkylphenol Method Information

Laboratory code	LAB15	LAB16	LAB17
Danube River Water	**Danube River Water**	**Danube River Water**	**Danube River Water**
Sample Volume [L]	1	1	1 l
Sampling method	bucket	bucket (metal)	Bucket, stainlss steel
Bottle type	glass	glass bottle	Glasbottle
Bottle preparation	solvent cleaning	pre-rinsing	pre-rinsing
Sample transport	ambient	cooled	cooled
Sample preservation	refrigerating	refrigerating	no preservation
Sample pretreatment and SPM separation	no	-	no pretreatment
Time between sampling and analysis	7 days	30 days	6 days
SPM Extraction technique:		-	
Water Extraction technique:	LLE	lle	LLE after derivatization with acetic anhydride
LLE	n-pentane	dichloromethane, pH=2 (H2SO4)	n-hexane
SPE cartridge		-	
SPE conditions		-	
Clean Up:	no	-	no clean up
SPE cartridge		-	
Derivatisation		N-(tBDMS)-N-(MTFA) with 1% tBDMSCl	acetic anhydride
GC column:	Rtx-5MS	Rtx-5Sil MS	Restek RTx-5Sil MS
Length	60	30m	30m x 0,25mm
Film thickness	0.25	0.25µm	0,25µm
Temperature program		oven: 50C(1m), 30C/m, 140C (0m), 10C/m, 320C (8m), injector: 50C(0.6m), 999C/min, 250C	85°(1min)-30°/min->150°-3°/min->207°-20°/min->300°
LC column:		-	
i.d. x lenght		-	
mobile phase		-	
Detector		-	
Wavelenghts		-	
GC/MS system:	Agilent 5973i; quadrupole	Perkin Elmer LR-MS	Agilent GC/MSD 5975
LC/MS system		-	
ions monitored	135; 177; 220	249, 263, 277, 320, 334	Nonylphenol: 260, 262; Octylphenol: 107, 206
LC/MS-MS transitions used		-	
Ionisation		EI	EI
ion suppression evaluated		-	
^{13}C/Deuterated Internal Standards		-	4-Nonylphenol D8, added to sample
^{13}C/Deuterated Recovery Standards		-	
		4-tert-Butylphenol	
Method:	EN 12673:1998	EPA 8151A	according to EN 12673
Measurement uncertainty(if available)		-	
Blank values		0	
Comments:	The quantification was made with your standard solution.	-	

(*): Specified filter type and cut-off size
(**): Specified adsorbent and/or solvent used

Table 13: Alkylphenol Method Information

Laboratory code	LAB2	LAB3
Extract E2	**Extract E2**	**Extract E2**
Clean Up: SPE cartridge Derivatisation	if different	Solvent exchange to toluene, then 1.5 g silica column (deactivated with milliQ water, 5% w/w); elution with toluene (45 mL) none none
GC column: Length Film thickness Temperature program		
LC column: i.d. x lenght mobile phase Detector Wavelenghts		
GC/MS system: LC/MS system ions monitored LC/MS-MS transitions used Ionisation ion suppression evaluated		
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards		^{13}C6 4-n-NP, added before clean-up
Method: Measurement uncertainty(if available) Blank values	 < LQ NP and OP	
  Comments:		 Stored at -20˚C in the dark until analysis

Laboratory code	LAB2	LAB3
Standard S3	**Standard S3**	**Standard S3**
Derivatisation	if different	none
GC column: Length Film thickness Temperature program		
LC column: i.d. x lenght mobile phase Detector Wavelenghts		
GC/MS system: LC/MS system ions monitored LC/MS-MS transitions used Ionisation ion suppression evaluated		
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards		^{13}C6 4-n-NP, added before injection in GC-MS
Method: Measurement uncertainty(if available) Blank values	 < LD NP and OP	
  Comments:		 Stored at -20˚C in the dark until analysis. Solvent exchanged to toluene before injection in GC-MS

Table 13: Alkylphenol Method Information

Laboratory code	LAB4	LAB4	LAB5	LAB6
Extract E2	**Extract E2**	**Extract E2**	**Extract E2**	**Extract E2**
Clean Up: SPE cartridge Derivatisation	if different	if different	dilution with water and further as above	if different
GC column: Length Film thickness Temperature program			DB-1 30m 0.25	
LC column: i.d. x lenght mobile phase Detector Wavelenghts				
GC/MS system: LC/MS system ions monitored LC/MS-MS transitions used Ionisation ion suppression evaluated			low res Agilent FullMS NCI	
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards				
Method: Measurement uncertainty(if available) Blank values				
  Comments:				

Laboratory code	LAB4	LAB4	LAB5	LAB6
Standard S3	**Standard S3**	**Standard S3**	**Standard S3**	**Standard S3**
Derivatisation	if different	if different	if different	if different
GC column: Length Film thickness Temperature program				
LC column: i.d. x lenght mobile phase Detector Wavelenghts				
GC/MS system: LC/MS system ions monitored LC/MS-MS transitions used Ionisation ion suppression evaluated				
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards				
Method: Measurement uncertainty(if available) Blank values				
  Comments:				

Table 13: Alkylphenol Method Information

Laboratory code	LAB7	LAB9	LAB10		LAB11
Extract E2	**Extract E2**	**Extract E2**	**Extract E2**		**Extract E2**
Clean Up: SPE cartridge Derivatisation		if different	if different		100 µl spiked in 80ML water, extr.as water sample
GC column: Length Film thickness Temperature program	DB-5 60m 0.25µm 70ºC 1min, 20ºC/min, 180ºC 1min, 5ºC/min, 310ºC 15min; Injection T. 270ºC				
LC column: i.d. x lenght mobile phase Detector Wavelenghts					
GC/MS system: LC/MS system ions monitored LC/MS-MS transitions used Ionisation ion suppression evaluated	MD-800, Low Resolution MS (SIM) 113, 135, 157, 179, 188, 189, 206, 223, 228, 270, 314 EI (70eV)				
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards	3, added before the analysis by GC/MS				
Method: Measurement uncertainty(if available) Blank values	EPA 1625				
  Comments:	LRMS SIM Method: 11 ions monitored in 1 functions (dwell time 50ms)				***compounds in extr. not derivatised***

Laboratory code	LAB7	LAB9	LAB10		LAB11
Standard S3	**Standard S3**	**Standard S3**	**Standard S3**		**Standard S3**
Derivatisation		if different	if different		100 µl spiked in 80ML water, extr.as water sample
GC column: Length Film thickness Temperature program	DB-5 60m 0.25µm 70ºC 1min, 20ºC/min, 180ºC 1min, 5ºC/min, 310ºC 15min; Injection T. 270ºC				
LC column: i.d. x lenght mobile phase Detector Wavelenghts					
GC/MS system: LC/MS system ions monitored LC/MS-MS transitions used Ionisation ion suppression evaluated	MD-800, Low Resolution MS (SIM) 113, 135, 157, 179, 188, 189, 206, 223, 228, 270, 314 EI (70eV)				
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards	3, added before the analysis by GC/MS				
Method: Measurement uncertainty(if available) Blank values	EPA 1625				
  Comments:	LRMS SIM Method: 11 ions monitored in 1 functions (dwell time 50ms)				***compounds in std. not derivatised***

Table 13: Alkylphenol Method Information

Laboratory code	LAB12	LAB13	LAB14
Extract E2	**Extract E2**	**Extract E2**	**Extract E2**
Clean Up: SPE cartridge Derivatisation		if different	silica column after derivatisation acetylation
GC column: Length Film thickness Temperature program			as above
LC column: i.d. x lenght mobile phase Detector Wavelenghts	HPLC system Agilent HP 1100, HPLC column LiChrosphere 4 mm x 12.5 cm, particle diameter 5um gradient elution; mobile phase A: 50% acetonitrile in methanol; B: 5% acetonitrile in water fluorescence detector Agilent HP 1200 Excitation/Emission = 232/310 nm		
GC/MS system: LC/MS system ions monitored LC/MS-MS transitions used Ionisation ion suppression evaluated			as above
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards			
Method: Measurement uncertainty(if available) Blank values			 NP 2 ng, OP 0,2 ng
Comments:	Because of the incompatibility of acetone with the HPLC mobile phase (shifting of peaks) the extract was evaporated using a gentle stream of nitrogen to dryness and redissolved in the same volume of acetonitrile. For HPLC analysis, undiluted extract was injected (15 ul)		

Laboratory code	LAB12	LAB13	LAB14
Standard S3	**Standard S3**	**Standard S3**	**Standard S3**
Derivatisation	if different	if different	acetylation
GC column: Length Film thickness Temperature program			as above
LC column: i.d. x lenght mobile phase Detector Wavelenghts	HPLC system Agilent HP 1100, HPLC column LiChrosphere 4 mm x 12.5 cm, particle diameter 5um gradient elution; mobile phase A: 50% acetonitrile in methanol; B: 5% acetonitrile in water fluorescence detector Agilent HP 1200 Excitation/Emission = 232/310 nm		
GC/MS system: LC/MS system ions monitored LC/MS-MS transitions used Ionisation ion suppression evaluated			as above
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards			
Method: Measurement uncertainty(if available) Blank values			
Comments:	Because of the incompatibility of acetone with the HPLC mobile phase (shifting of peaks) the extract was evaporated using a gentle stream of nitrogen to dryness and redissolved in the same volume of acetonitrile. For HPLC analysis, undiluted extract was injected (15 ul)		

Table 13: Alkylphenol Method Information

Laboratory code	LAB15	LAB16	LAB17
Extract E2	**Extract E2**	**Extract E2**	**Extract E2**
Clean Up: SPE cartridge Derivatisation	if different	if different	if different
GC column: Length Film thickness Temperature program			
LC column: i.d. x lenght mobile phase Detector Wavelenghts			
GC/MS system: LC/MS system ions monitored LC/MS-MS transitions used Ionisation ion suppression evaluated			
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards			
Method: Measurement uncertainty(if available) Blank values			
Comments:			The extract was added to 1 l tap water; then the spiked water was treated as described above (derivatization, LLE).

Laboratory code	LAB15	LAB16	LAB17
Standard S3	**Standard S3**	**Standard S3**	**Standard S3**
Derivatisation	if different	if different	if different
GC column: Length Film thickness Temperature program			
LC column: i.d. x lenght mobile phase Detector Wavelenghts			
GC/MS system: LC/MS system ions monitored LC/MS-MS transitions used Ionisation ion suppression evaluated			
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards			
Method: Measurement uncertainty(if available) Blank values			
Comments:			The extract was added to 1 l tap water; then the spiked water was treated as described above (derivatization, LLE).

Annex II

Reported results from all CMA-onsite 2 participants

Table 14: Summary of reported PAH Data

Laboratory code	LAB1	LAB1	LAB2
Standard S2	**Standard S2**		**Standard S2**
Unit	(ng/ml)		(ng/ml)
Date Received:			22/09/08
Volume Analysed:	0.5 mL		0,191 mL
Date Analysed:			24/09/08
Anthracene	19.6		22.0
Fluoranthene	74.0		83.3
Benzo(a)pyrene	28.7		41.1
Benzo(b)fluoranthene	41.1		48.7
Benzo(k)fluoranthene	37.9		47.5
Benzo(b+j+k)fluoranthene*			
Benzo(g,h,i)perylene	34.7		33.5
Indeno(1,2,3-cd)pyrene	37.2		42.9

Extract E1	**Extract E1**		**Extract E1**
Unit	(ng/ml)		(ng/ml)
Date Received:			22/09/08
Volume Analysed:	0.5 mL		0,101 mL
Date Analysed:			24/09/08
Anthracene	5.8		14.6
Fluoranthene	58.0		90.9
Benzo(a)pyrene	19.8		30.4
Benzo(b)fluoranthene	29.4		29.3
Benzo(k)fluoranthene	9.9		16.0
Benzo(b+j+k)fluoranthene*			
Benzo(g,h,i)perylene	16.8		22.4
Indeno(1,2,3-cd)pyrene	16.8		25.2

Table 14: Summary of reported PAH Data

Laboratory code	LAB3	LAB4	LAB5
Standard S2	**Standard S2**	**Standard S2**	**Standard S2**
Unit	(ng/ml)	(ng/ml)	(ng/ml)
Date Received:	22/09/08	23/09/08	01/10/08
Volume Analysed:	0,200 ml	0,50ml	
Date Analysed:	09/10/08	29/09/09	07/10/08
Anthracene	17.7	11	10.6
Fluoranthene	69.4	51	42.6
Benzo(a)pyrene	27.3	21	104
Benzo(b)fluoranthene	38.2	30	43.9
Benzo(k)fluoranthene	37.1	27	42.6
Benzo(b+j+k)fluoranthene*			*
Benzo(g,h,i)perylene	24.2	19	37.5
Indeno(1,2,3-cd)pyrene	21.7	19	44.7

Extract E1	**Extract E1**	**Extract E1**	**Extract E1**
Unit	(ng/ml)	(ng/ml)	(ng/ml)
Date Received:	22/09/08	23/09/08	01/10/08
Volume Analysed:	0,200 ml	0,50ml	
Date Analysed:	09/10/08	29/09/09	07/10/08
Anthracene	2.7	4.2	4.05
Fluoranthene	43.5	53	34.2
Benzo(a)pyrene	16.6	17	10.4
Benzo(b)fluoranthene	16.6	22	20
Benzo(k)fluoranthene	7.0	10	9.2
Benzo(b+j+k)fluoranthene*			*
Benzo(g,h,i)perylene	17.8	20	15.5
Indeno(1,2,3-cd)pyrene	10.0	15	21

Table 14: Summary of reported PAH Data

Laboratory code	LAB6	LAB7	LAB8	LAB8
Standard S2	**Standard S2**	**Standard S2**	**Standard S2**	
Unit	(ng/ml)	(ng/ml)	(ng/ml)	
Date Received:	23/09/08	23/09/2008	22/09/08	
Volume Analysed:	100µl	1.2 mL	0,1 mL	
Date Analysed:	24/09/08	09/10/08	10/10/08	
Anthracene	16.7	23.7	39,7± 0,9	
Fluoranthene	74.3	63.7	149±3	
Benzo(a)pyrene	<0,5	37.6	72±2	
Benzo(b)fluoranthene	121.5	49.1	93±2	
Benzo(k)fluoranthene	16.1	48.1	102,81±2,05	
Benzo(b+j+k)fluoranthene*				
Benzo(g,h,i)perylene	<0,5	39.8	72±2	
Indeno(1,2,3-cd)pyrene	35.9	45.5	61±1	

Extract E1	**Extract E1**	**Extract E1**	**Extract E1**	
Unit	(ng/ml)	(ng/ml)	(ng/ml)	
Date Received:	23/09/08	23/09/2008	22/09/08	
Volume Analysed:	250µl	0.6 mL	0,1 mL	
Date Analysed:	24/09/08	10/09/08	10/10/08	
Anthracene	3.6	5.7	20,0±0,5	
Fluoranthene	5.6	70.8	104±2	
Benzo(a)pyrene	17.2	22	34,7±0,8	
Benzo(b)fluoranthene	22.1	24.9	37,5±0,9	
Benzo(k)fluoranthene	8.2	23.2	21,0±0,5	
Benzo(b+j+k)fluoranthene*				
Benzo(g,h,i)perylene	13.6	25	30,9±0,7	
Indeno(1,2,3-cd)pyrene	25.1	31.1	26,7±0,7	

Table 14: Summary of reported PAH Data

Laboratory code	LAB9	LAB10	LAB11	LAB12
Standard S2	**Standard S2**	**Standard S2**	**Standard S2**	**Standard S2**
Unit	(ng/ml)	(ng/ml)	(ng/ml)	(ng/ml)
Date Received:	23/09/08	13/11/08	23/09/08	18.9.2008
Volume Analysed:	1 µl	500 µL		15 ul
Date Analysed:	24/11/08	27/11/08	24/11/08	
Anthracene	17.2	< 10	25	not analysed
Fluoranthene	65.1	53	179	68
Benzo(a)pyrene	21.5	30	131	32.6
Benzo(b)fluoranthene	36.4	40	-	49.7
Benzo(k)fluoranthene	31.5	39	-	41.35
Benzo(b+j+k)fluoranthene*		-	319	
Benzo(g,h,i)perylene	24.3	32	142	31.5
Indeno(1,2,3-cd)pyrene	23.7	32	126	38.8

Extract E1	**Extract E1**	**Extract E1**	**Extract E1**	**Extract E1**
Unit	(ng/ml)	(ng/ml)	(ng/ml)	(ng/ml)
Date Received:	23/09/08	13/11/08	23/09/08	18.9.2008
Volume Analysed:	1 µl	500 µL		15 ul
Date Analysed:	24/11/08	27/11/08	24/11/08	
Anthracene	4.8	< 10	43	not analysed
Fluoranthene	68.9	78	187	62
Benzo(a)pyrene	25.2	28	301	10.3
Benzo(b)fluoranthene	27.4	55	-	17.25
Benzo(k)fluoranthene	20.8	19	-	not detected
Benzo(b+j+k)fluoranthene*		-	278	
Benzo(g,h,i)perylene	19.8	37	119	8.45
Indeno(1,2,3-cd)pyrene	26.1	28	116	8.45

Table 14: Summary of reported PAH Data

Laboratory code	LAB13	LAB14	LAB15	LAB16
Standard S2	**Standard S2**	**Standard S2**	**Standard S2**	**Standard S2**
Unit	(ng/ml)	(ng/ml)	(ng/ml)	(ng/ml)
Date Received:	18/09/08	Could not be analysed on HPLC	19-Sep	18.9.08
Volume Analysed:	50 µL	because extract was in nonane	1 ml	100µl
Date Analysed:	04/11/08		07-Oct	8.10.08
Anthracene	21.8		9.3	18
Fluoranthene	68.3		67.2	95
Benzo(a)pyrene	36.7		56.7	44
Benzo(b)fluoranthene	48.8		71.3	54
Benzo(k)fluoranthene	50.9		67.5	54
Benzo(b+j+k)fluoranthene*				-
Benzo(g,h,i)perylene	40.7		51.1	43
Indeno(1,2,3-cd)pyrene	22.5		52.8	35

Extract E1	**Extract E1**	**Extract E1**	**Extract E1**	**Extract E1**
Unit	(ng/ml)	(ng/ml)	(ng/ml)	~~(ng/ml)~~ **ng/sample**
Date Received:	18/09/08	30/09/08	19-Sep	18.9.08
Volume Analysed:	50 µL	0.60	total	all
Date Analysed:	11/11/08	02/12/08	07-Oct	8.10.08
Anthracene	3.9	3.1	6.2	3
Fluoranthene	58.9	63	51.6	37.7
Benzo(a)pyrene	20.2	23	27.0	17.1
Benzo(b)fluoranthene	22.0	27	37.0	36.1
Benzo(k)fluoranthene	11.7	13	14.5	11
Benzo(b+j+k)fluoranthene*				-
Benzo(g,h,i)perylene	21.4	25	20.1	8.9
Indeno(1,2,3-cd)pyrene	<LOD	19	19.9	7.9

Table 14: Summary of reported PAH Data

Laboratory code	LAB16	LAB17	LAB18	LAB19
Standard S2	**Standard S2**	**Standard S2**	**Standard S2**	**Standard S2**
Unit	(ng/ml)	(ng/ml)	(ng/ml)	(ng/ml)
Date Received:	18.9.08	22/09/08	20.09.2008.	18/09/08
Volume Analysed:	500µl	28/10/08	2µL	20µL
Date Analysed:	18.11.08	28/10/08	19.11.2008.	30/09/08
Anthracene	18	17	18.700	19
Fluoranthene	41	84	62.210	59.5
Benzo(a)pyrene	39	38	42.700	46.9
Benzo(b)fluoranthene	44	51	48.600	
Benzo(k)fluoranthene	43	52	46.700	
Benzo(b+j+k)fluoranthene*	-	103		81.1
Benzo(g,h,i)perylene	50	42	40.620	22.8
Indeno(1,2,3-cd)pyrene	39	41	46.000	22

Extract E1	**Extract E1**	**Extract E1**	**Extract E1**	**Extract E1**
Unit	~~(ng/ml)~~ **ng/sample**	(ng/ml)	(ng/ml)	(ng/ml)
Date Received:	18.9.08	22/09/08	20.09.2008.	18/09/08
Volume Analysed:	all	28/10/08	2µL	20µL
Date Analysed:	18.11.08	28/10/08	20.11.2008.	30/09/08
Anthracene	1.8	3	5.285	6.8
Fluoranthene	40.9	42	66.000	48.3
Benzo(a)pyrene	12	15	29.730	21.8
Benzo(b)fluoranthene	18.5	26	31.310	
Benzo(k)fluoranthene	5.5	8	28.100	
Benzo(b+j+k)fluoranthene*	-	34		39.1
Benzo(g,h,i)perylene	7.6	13	25.825	14.4
Indeno(1,2,3-cd)pyrene	6.4	14	32.910	10.1

Table 14: Summary of reported PAH Data

Laboratory code	LAB20	LAB21	LAB22
Standard S2	**Standard S2**	**Standard S2**	**Standard S2**
Unit	(ng/ml)	(ng/ml)	(ng/ml)
Date Received:	22. 09. 2008.	19.09.2008	20/09/08
Volume Analysed:	0,5 L	total	1 ml
Date Analysed:	24. 11. 2008.	24.09.2008.	14/10/08
Anthracene	17	24	30.95
Fluoranthene	75	81	84.06
Benzo(a)pyrene	64	60	40.69
Benzo(b)fluoranthene	81	62	62.66
Benzo(k)fluoranthene	80	65	57.01
Benzo(b+j+k)fluoranthene*			119.67
Benzo(g,h,i)perylene	64	40	4.53
Indeno(1,2,3-cd)pyrene	68	40	95.58

Extract E1	**Extract E1**	**Extract E1**	**Extract E1**
Unit	(ng/ml)	(ng/ml)	(ng/ml)
Date Received:	22. 09. 2008.	19.09.2008	20/09/08
Volume Analysed:	0,5 L	0,6 ml	1 ml
Date Analysed:	24. 11. 2008.	24.09.2008.	14/10/08
Anthracene	4	6	4.38
Fluoranthene	53	54	68.2
Benzo(a)pyrene	26	28	22.75
Benzo(b)fluoranthene	30	30	38.33
Benzo(k)fluoranthene	29	15	16.32
Benzo(b+j+k)fluoranthene*			54.65
Benzo(g,h,i)perylene	28	20	46.8
Indeno(1,2,3-cd)pyrene	32	23	12.77

Table 14: Summary of reported PAH Data

Laboratory code	LAB1	LAB1	LAB2
Danube dissolved conc.* **	**Danube dissolved conc.*** **	**Danube dissolved conc.*** **	**Danube dissolved conc.*** **
Unit	(ng/l)	(ng/l)	(ng/l)
Date Received: Volume Analysed: Date Analysed:			
Anthracene		0.12	
Fluoranthene		0.98	
Benzo(a)pyrene		0.01	
Benzo(b)fluoranthene		0.01	
Benzo(k)fluoranthene		0.00	
Benzo(b+j+k)fluoranthene*			
Benzo(g,h,i)perylene		0.03	
Indeno(1,2,3-cd)pyrene		0.00	

Danube SPM conc.* **	**Danube SPM conc.*** **	**Danube SPM conc.*** **	**Danube SPM conc.*** **
Unit	(ng/l)	(ng/l)	(ng/l)
Date Received: Volume Analysed: Date Analysed:			
Anthracene		0.35	
Fluoranthene		1.66	
Benzo(a)pyrene		0.74	
Benzo(b)fluoranthene		1.20	
Benzo(k)fluoranthene		0.42	
Benzo(b+j+k)fluoranthene*			
Benzo(g,h,i)perylene		0.70	
Indeno(1,2,3-cd)pyrene		0.74	

Danube whole water conc.	**Danube whole water conc.**	**Danube whole water conc.**	**Danube whole water conc.**
Unit	(ng/l)	(ng/l)	(ng/l)
Date Received: Volume Analysed: Date Analysed:	2.3 L	29.1 L	19/09/08 9 L 22/09/08
Anthracene	0.48	0.47	1.0
Fluoranthene	3.08	2.65	1.3
Benzo(a)pyrene	0.69	0.75	1.0
Benzo(b)fluoranthene	1.25	1.22	1.0
Benzo(k)fluoranthene	0.43	0.43	0.5
Benzo(b+j+k)fluoranthene*			
Benzo(g,h,i)perylene	0.78	0.73	0.3
Indeno(1,2,3-cd)pyrene	0.79	0.75	0.8

Table 14: Summary of reported PAH Data

Laboratory code	LAB3	LAB4	LAB5
Danube dissolved conc.* **	**Danube dissolved conc.*** **	**Danube dissolved conc.*** **	**Danube dissolved conc.*** **
Unit	(ng/l)	(ng/l)	(ng/l)
Date Received: Volume Analysed: Date Analysed:			
Anthracene **Fluoranthene** **Benzo(a)pyrene** **Benzo(b)fluoranthene** **Benzo(k)fluoranthene** **Benzo(b+j+k)fluoranthene*** **Benzo(g,h,i)perylene** **Indeno(1,2,3-cd)pyrene**			

Danube SPM conc.* **	**Danube SPM conc.*** **	**Danube SPM conc.*** **	**Danube SPM conc.*** **
Unit	(ng/l)	(ng/l)	(ng/l)
Date Received: Volume Analysed: Date Analysed:			
Anthracene **Fluoranthene** **Benzo(a)pyrene** **Benzo(b)fluoranthene** **Benzo(k)fluoranthene** **Benzo(b+j+k)fluoranthene*** **Benzo(g,h,i)perylene** **Indeno(1,2,3-cd)pyrene**			

Danube whole water conc.	**Danube whole water conc.**	**Danube whole water conc.**	**Danube whole water conc.**
Unit	(ng/l)	(ng/l)	(ng/l)
Date Received:	22/09/08	19/09/08	22/09/08
Volume Analysed:	1 L	1 l	
Date Analysed:	24/09/08	22/09/08	07/10/08
Anthracene	<LOQ	0.59	< 10
Fluoranthene	2.3	3.2	< 10
Benzo(a)pyrene	0.4	0.45	< 10
Benzo(b)fluoranthene	0.6	0.67	2.3
Benzo(k)fluoranthene	0.3	0.34	< 1
Benzo(b+j+k)fluoranthene*			
Benzo(g,h,i)perylene	0.4	0.59	1.2
Indeno(1,2,3-cd)pyrene	<LOQ	<1	1.3

Table 14: Summary of reported PAH Data

Laboratory code	LAB6	LAB7	LAB8	LAB8
Danube dissolved conc.* **	**Danube dissolved conc.*** **	**Danube dissolved conc.*** **	**Danube dissolved conc.*** **	**Danube dissolved conc.*** **
Unit	(ng/l)	(ng/l)	(ng/l)	(ng/l)
Date Received:			19/09/08	19/09/08
Volume Analysed:			2,5 L	2,5 L
Date Analysed:			24/09/08	24/09/08
Anthracene			0,56±0,02	0,47±0,02
Fluoranthene			3,1±0,1	5,6±0,2
Benzo(a)pyrene			0,050±0,003	0,057±0,003
Benzo(b)fluoranthene			0,19±0,01	0,128±0,007
Benzo(k)fluoranthene			0,088±0,005	0,069±0,004
Benzo(b+j+k)fluoranthene*				
Benzo(g,h,i)perylene			0,19±0,01	0,150±0,008
Indeno(1,2,3-cd)pyrene			0,100±0,006	0,052±0,003

Danube SPM conc.* **	**Danube SPM conc.*** **	**Danube SPM conc.*** **	**Danube SPM conc.*** **	**Danube SPM conc.*** **
Unit	(ng/l)	(ng/l)	(ng/l)	(ng/l)
Date Received:			19/09/08	19/09/08
Volume Analysed:			2,5 L	2,5 L
Date Analysed:			24/09/08	24/09/08
Anthracene			1,10±0,04	1,10±0,04
Fluoranthene			10,7±0,3	10,3±0,3
Benzo(a)pyrene			3,2±0,1	2,25±0,08
Benzo(b)fluoranthene			5,1±0,2	4,5±0,1
Benzo(k)fluoranthene			2,8±0,1	2,37±0,08
Benzo(b+j+k)fluoranthene*				
Benzo(g,h,i)perylene			2,49±0,09	2,18±0,08
Indeno(1,2,3-cd)pyrene			2,16±0,08	1,77±0,07

Danube whole water conc.	**Danube whole water conc.**	**Danube whole water conc. #**	**Danube whole water conc.**	
Unit	(ng/l)	(ng/l)	(ng/l)	
Date Received:	19/09/08	26/09/2008		
Volume Analysed:	2 L	1 L		
Date Analysed:	24/09/08	29/09/2008		
Anthracene	<0,25	< 0.2		
Fluoranthene	1.1	3.1		
Benzo(a)pyrene	0.35	< 0.9		
Benzo(b)fluoranthene	0.39	0.5		
Benzo(k)fluoranthene	<0,25	0.3		
Benzo(b+j+k)fluoranthene*				
Benzo(g,h,i)perylene	0.31	< 0.3		
Indeno(1,2,3-cd)pyrene	0.53	< 0.7		

Table 14: Summary of reported PAH Data

Laboratory code	LAB9	LAB10	LAB11	LAB12
Danube dissolved conc.* **	**Danube dissolved conc.*** **	**Danube dissolved conc.*** **	**Danube dissolved conc.*** **	**Danube dissolved conc.*** **
Unit	(ng/l)	(ng/l)	(ng/l)	(ng/l)
Date Received:				not analysed
Volume Analysed:				not analysed
Date Analysed:				not analysed
Anthracene				not analysed
Fluoranthene				not analysed
Benzo(a)pyrene				not analysed
Benzo(b)fluoranthene				not analysed
Benzo(k)fluoranthene				not analysed
Benzo(b+j+k)fluoranthene*				not analysed
Benzo(g,h,i)perylene				not analysed
Indeno(1,2,3-cd)pyrene				not analysed

Danube SPM conc.* **	**Danube SPM conc.*** **	**Danube SPM conc.*** **	**Danube SPM conc.*** **	**Danube SPM conc.*** **
Unit	(ng/l)	(ng/g) --> (ng/L with TSM 14 mg/L)	(ng/l)	(ng/l)
Date Received:		13/11/08		not analysed
Volume Analysed:		1 g --> 71.4 L		not analysed
Date Analysed:		27/11/08		not analysed
Anthracene		< 10 --> < 0.14		not analysed
Fluoranthene		86 --> 1.21		not analysed
Benzo(a)pyrene		35 --> 0.49		not analysed
Benzo(b)fluoranthene		57 --> 0.8		not analysed
Benzo(k)fluoranthene		22 --> 0.31		not analysed
Benzo(b+j+k)fluoranthene*		-		not analysed
Benzo(g,h,i)perylene		< 10 --> < 0.14		not analysed
Indeno(1,2,3-cd)pyrene		< 10 --> < 0.14		not analysed

Danube whole water conc.	**Danube whole water conc.**	**Danube whole water conc.**	**Danube whole water conc.**	**Danube whole water conc.**
Unit	(ng/l)	(ng/l)	(ng/l)	(ng/l)
Date Received:	22/09/08	13/11/08	23/09/08	18.9.2008
Volume Analysed:	2000 ml	1 L	10 liter	1 L
Date Analysed:	24/09/08	27/11/08	03/11/08	water extracted 22.9.2008
Anthracene	< 3	< 10	0.39	<5.0
Fluoranthene	< 3	< 10	6.75	<5.0
Benzo(a)pyrene	< 1	< 10	1.13	<2.0
Benzo(b)fluoranthene	< 3	< 10	1.01	<5.0
Benzo(k)fluoranthene	< 3	< 10	0.59	<5.0
Benzo(b+j+k)fluoranthene*		-	-	
Benzo(g,h,i)perylene	< 3	< 10	0.74	<2.0
Indeno(1,2,3-cd)pyrene	< 3	< 10	0.78	<2.0

Table 14: Summary of reported PAH Data

Laboratory code	LAB13	LAB14	LAB15	LAB16
Danube dissolved conc.* **	**Danube dissolved conc.*** **	**Danube dissolved conc.*** **	**Danube dissolved conc.*** **	**Danube dissolved conc.*** **
Unit	(ng/l)	(ng/l)	(ng/l)	(ng/l)
Date Received:		30/09/08		
Volume Analysed:		4L		
Date Analysed:		02/12/08		
Anthracene		0.09		
Fluoranthene		1.2		
Benzo(a)pyrene				
Benzo(b)fluoranthene				
Benzo(k)fluoranthene				
Benzo(b+j+k)fluoranthene*				
Benzo(g,h,i)perylene				
Indeno(1,2,3-cd)pyrene				

Danube SPM conc.* **	**Danube SPM conc.*** **	**Danube SPM conc.*** **	**Danube SPM conc.*** **	**Danube SPM conc.*** **
Unit	(ng/l)	(ng/l)	(ng/l)	(ng/l)
Date Received:		30/09/08		
Volume Analysed:		4L		
Date Analysed:		02/12/08		
Anthracene		0.19		
Fluoranthene		10		
Benzo(a)pyrene		1.5		
Benzo(b)fluoranthene		2.6		
Benzo(k)fluoranthene		1.1		
Benzo(b+j+k)fluoranthene*				
Benzo(g,h,i)perylene		1.4		
Indeno(1,2,3-cd)pyrene		1.2		

Danube whole water conc.	**Danube whole water conc.**	**Danube whole water conc.**	**Danube whole water conc.**	**Danube whole water conc.**
Unit	(ng/l)	(ng/l)	(ng/l)	(ng/l)
Date Received:	18/09/08	30/09/08	19-Sep	18.9.08
Volume Analysed:	50 µL	4L	1 liter	1000 ml
Date Analysed:	27/10/08	02/12/08	07-Oct	8.10.08
Anthracene	4	0.28	0.69	<10
Fluoranthene	15	11	3.89	<10
Benzo(a)pyrene	5	1.5	1.30	<10
Benzo(b)fluoranthene	14	2.6	2.87	<10
Benzo(k)fluoranthene	6.9	1.1	1.11	<10
Benzo(b+j+k)fluoranthene*				<10
Benzo(g,h,i)perylene	7	1.4	1.34	<10
Indeno(1,2,3-cd)pyrene	10	1.2	1.78	<10

Table 14: Summary of reported PAH Data

Laboratory code	LAB16	LAB17	LAB18	LAB19
Danube dissolved conc.* **		**Danube dissolved conc.*** **	**Danube dissolved conc.*** **	**Danube dissolved conc.*** **
Unit		(ng/l)	(ng/l)	(ng/l)
Date Received: Volume Analysed: Date Analysed:				
Anthracene **Fluoranthene** **Benzo(a)pyrene** **Benzo(b)fluoranthene** **Benzo(k)fluoranthene** **Benzo(b+j+k)fluoranthene*** **Benzo(g,h,i)perylene** **Indeno(1,2,3-cd)pyrene**				

Danube SPM conc.* **		**Danube SPM conc.*** **	**Danube SPM conc.*** **	**Danube SPM conc.*** **
Unit		(ng/l)	(ng/l)	(ng/l)
Date Received: Volume Analysed: Date Analysed:				
Anthracene **Fluoranthene** **Benzo(a)pyrene** **Benzo(b)fluoranthene** **Benzo(k)fluoranthene** **Benzo(b+j+k)fluoranthene*** **Benzo(g,h,i)perylene** **Indeno(1,2,3-cd)pyrene**				

Danube whole water conc.	**Danube whole water c.**	**Danube whole water conc.**	**Danube whole water conc.**	**Danube whole water conc.**
Unit	(ng/l)	(ng/l)	(ng/l)	(ng/l)
Date Received:	18.9.08	22/09/08	20.09.2008.	18/09/08
Volume Analysed:	1000 ml	28/10/08	2µL	20µL
Date Analysed:	8.10.08	28/10/08	21.11.2008.	30/09/08
Anthracene	<10	< 2	0.450	<3
Fluoranthene	<10	< 2	4.350	4.1
Benzo(a)pyrene	<10	< 2	0.780	<3
Benzo(b)fluoranthene	<10	< 2	1.115	
Benzo(k)fluoranthene	<10	< 2	0.820	
Benzo(b+j+k)fluoranthene*	<10			<3
Benzo(g,h,i)perylene	<10	< 2	0.850	<1
Indeno(1,2,3-cd)pyrene	<10	< 2	1.060	<1

Table 14: Summary of reported PAH Data

Laboratory code	LAB20	LAB21	LAB22
Danube dissolved conc.* **	**Danube dissolved conc.*** **	**Danube dissolved conc.*** **	**Danube dissolved conc.*** **
Unit	(ng/l)	(ng/l)	(ng/l)
Date Received: Volume Analysed: Date Analysed:			
Anthracene **Fluoranthene** **Benzo(a)pyrene** **Benzo(b)fluoranthene** **Benzo(k)fluoranthene** **Benzo(b+j+k)fluoranthene*** **Benzo(g,h,i)perylene** **Indeno(1,2,3-cd)pyrene**			

Danube SPM conc.* **	**Danube SPM conc.*** **	**Danube SPM conc.*** **	**Danube SPM conc.*** **
Unit	(ng/l)	(ng/l)	(ng/l)
Date Received: Volume Analysed: Date Analysed:			
Anthracene **Fluoranthene** **Benzo(a)pyrene** **Benzo(b)fluoranthene** **Benzo(k)fluoranthene** **Benzo(b+j+k)fluoranthene*** **Benzo(g,h,i)perylene** **Indeno(1,2,3-cd)pyrene**			

Danube whole water conc.	**Danube whole water conc.**	**Danube whole water conc.**	**Danube whole water conc.**
Unit	(ng/l)	(ng/l)	(ng/l)
Date Received:	22. 09. 2008.	19.09.2008	20/09/08
Volume Analysed:	0,5 L	1,0 liter	1 ml
Date Analysed:	24. 11. 2008.	24.09.2008.	14/10/08
Anthracene	1	1.5	<1
Fluoranthene	1.3	10	7.41
Benzo(a)pyrene	1	1.2	2.09
Benzo(b)fluoranthene	1	2	3.29
Benzo(k)fluoranthene	1	2	6.2
Benzo(b+j+k)fluoranthene*			9.49
Benzo(g,h,i)perylene	0.4	1	3.05
Indeno(1,2,3-cd)pyrene	1.2	1	1.98

Table 14: Summary of reported PAH Data

Laboratory code	LAB1	LAB1	LAB2
LOQ Dissolved***	**LOQ** Dissolved***	**LOQ** Dissolved***	**LOQ** Dissolved***
Unit	(ng/l)	(ng/l)	(ng/l)
Anthracene		0.01	
Fluoranthene		0.01	
Benzo(a)pyrene		0.001	
Benzo(b)fluoranthene		0.001	
Benzo(k)fluoranthene		0.001	
Benzo(b+j+k)fluoranthene*			
Benzo(g,h,i)perylene		0.001	
Indeno(1,2,3-cd)pyrene		0.001	

LOQ SPM***	**LOQ** SPM***	**LOQ** SPM***	**LOQ** SPM***
Unit	(ng/l)	(ng/l)	(ng/l)
Anthracene		0.02	
Fluoranthene		0.02	
Benzo(a)pyrene		0.002	
Benzo(b)fluoranthene		0.002	
Benzo(k)fluoranthene		0.002	
Benzo(b+j+k)fluoranthene*			
Benzo(g,h,i)perylene		0.002	
Indeno(1,2,3-cd)pyrene		0.002	

LOQ Whole Water**	**LOQ** Whole Water**	**LOQ** Whole Water**	**LOQ** Whole Water**
Unit	(ng/l)	(ng/l)	(ng/l)
Anthracene	0.04	0.03	0.2
Fluoranthene	0.03	0.03	0.2
Benzo(a)pyrene	0.01	0.003	0.2
Benzo(b)fluoranthene	0.01	0.003	0.2
Benzo(k)fluoranthene	0.01	0.003	0.2
Benzo(b+j+k)fluoranthene*			
Benzo(g,h,i)perylene	0.01	0.003	0.2
Indeno(1,2,3-cd)pyrene	0.01	0.003	0.2

(*): If your chromatographic method does not perform the separation of the Benzo-fluoranthene isomers report the sum of them
(**): LOQ for the method applied for water analysis.
(***): Fill the corresponding column if fractions have been analysed spearately

Table 14: Summary of reported PAH Data

Laboratory code	LAB3	LAB4	LAB5
LOQ Dissolved***	**LOQ** Dissolved***	**LOQ** Dissolved***	**LOQ** Dissolved***
Unit	(ng/l)	(ng/l)	(ng/l)
Anthracene			
Fluoranthene			
Benzo(a)pyrene			
Benzo(b)fluoranthene			
Benzo(k)fluoranthene			
Benzo(b+j+k)fluoranthene*			
Benzo(g,h,i)perylene			
Indeno(1,2,3-cd)pyrene			

LOQ SPM***	**LOQ** SPM***	**LOQ** SPM***	**LOQ** SPM***
Unit	(ng/l)	(ng/l)	(ng/l)
Anthracene			
Fluoranthene			
Benzo(a)pyrene			
Benzo(b)fluoranthene			
Benzo(k)fluoranthene			
Benzo(b+j+k)fluoranthene*			
Benzo(g,h,i)perylene			
Indeno(1,2,3-cd)pyrene			

LOQ Whole Water**	**LOQ** Whole Water**	**LOQ** Whole Water**	**LOQ** Whole Water**
Unit	(ng/l)	(ng/l)	(ng/l)
Anthracene	0.2	0.25	< 10
Fluoranthene	0.2	0.5	< 10
Benzo(a)pyrene	0.2	0.25	< 10
Benzo(b)fluoranthene	0.2	0.25	< 1
Benzo(k)fluoranthene	0.2	0.25	< 1
Benzo(b+j+k)fluoranthene*			*
Benzo(g,h,i)perylene	0.2	0.5	1.2
Indeno(1,2,3-cd)pyrene	0.2	1	1.3

(*): If your chromatographic methoc
(**): LOQ for the method applied fo
(***): Fill the corresponding column

Table 14: Summary of reported PAH Data

Laboratory code	LAB6	LAB7	LAB8	LAB8
LOQ Dissolved***	**LOQ** Dissolved***	**LOQ** Dissolved***	**LOQ** Dissolved***	**LOQ** Dissolved***
Unit	(ng/l)	(ng/l)	(ng/l)	(ng/l)
Anthracene			0.03	0.04
Fluoranthene			0.08	0.10
Benzo(a)pyrene			0.07	0.03
Benzo(b)fluoranthene			0.07	0.03
Benzo(k)fluoranthene			0.07	0.03
Benzo(b+j+k)fluoranthene*				
Benzo(g,h,i)perylene			0.05	0.04
Indeno(1,2,3-cd)pyrene			0.05	0.04

LOQ SPM***	**LOQ** SPM***	**LOQ** SPM***	**LOQ** SPM***	**LOQ** SPM***
Unit	(ng/l)	(ng/l)	(ng/l)	(ng/l)
Anthracene			0.11	0.24
Fluoranthene			0.07	0.06
Benzo(a)pyrene			0.08	0.07
Benzo(b)fluoranthene			0.08	0.07
Benzo(k)fluoranthene			0.08	0.07
Benzo(b+j+k)fluoranthene*				
Benzo(g,h,i)perylene			0.12	0.11
Indeno(1,2,3-cd)pyrene			0.12	0.11

LOQ Whole Water**	**LOQ** Whole Water**	**LOQ** Whole Water**	**LOQ** Whole Water**	
Unit	(ng/l)	(ng/l)	(ng/l)	
Anthracene	0.25	0.2		
Fluoranthene	0.25	0.2		
Benzo(a)pyrene	0.25	0.9		
Benzo(b)fluoranthene	0.25	0.3		
Benzo(k)fluoranthene	0.25	0.3		
Benzo(b+j+k)fluoranthene*				
Benzo(g,h,i)perylene	0.25	0.3		
Indeno(1,2,3-cd)pyrene	0.25	0.7		

(*): If your chromatographic methoc
(**): LOQ for the method applied fo
(***): Fill the corresponding column

Table 14: Summary of reported PAH Data

Laboratory code	LAB9	LAB10	LAB11	LAB12
LOQ Dissolved***	**LOQ** Dissolved***	**LOQ** Dissolved***	**LOQ** Dissolved***	**LOQ** Dissolved***
Unit	(ng/l)	(ng/l)	(ng/l)	(ng/l)
Anthracene				not analysed
Fluoranthene				not analysed
Benzo(a)pyrene				not analysed
Benzo(b)fluoranthene				not analysed
Benzo(k)fluoranthene				not analysed
Benzo(b+j+k)fluoranthene*				not analysed
Benzo(g,h,i)perylene				not analysed
Indeno(1,2,3-cd)pyrene				not analysed

LOQ SPM***	**LOQ** SPM***	**LOQ** SPM***	**LOQ** SPM***	**LOQ** SPM***
Unit	(ng/l)	(ng/g)	(ng/l)	(ng/l)
Anthracene		10		not determined
Fluoranthene		10		not determined
Benzo(a)pyrene		10		not determined
Benzo(b)fluoranthene		10		not determined
Benzo(k)fluoranthene		10		not determined
Benzo(b+j+k)fluoranthene*		-		not determined
Benzo(g,h,i)perylene		10		not determined
Indeno(1,2,3-cd)pyrene		10		not determined

LOQ Whole Water**	**LOQ** Whole Water**	**LOQ** Whole Water**	**LOQ** Whole Water**	**LOQ** Whole Water**
Unit	(ng/l)	(ng/l)	(ng/l)	(ng/l)
Anthracene	< 3	10	1.24	5
Fluoranthene	< 3	10	5.65	5
Benzo(a)pyrene	< 1	10	0.91	2
Benzo(b)fluoranthene	< 3	10	1.16	5
Benzo(k)fluoranthene	< 3	10	0.49	5
Benzo(b+j+k)fluoranthene*		-	-	
Benzo(g,h,i)perylene	< 2	10	0.73	2
Indeno(1,2,3-cd)pyrene	< 2	10	0.87	2

(*): If your chromatographic methoc
(**): LOQ for the method applied fo
(***): Fill the corresponding column

Table 14: Summary of reported PAH Data

Laboratory code	LAB13	LAB14	LAB15	LAB16
LOQ Dissolved***	**LOQ** Dissolved***	**LOQ** Dissolved***	**LOQ** Dissolved***	**LOQ** Dissolved***
Unit	(ng/l)	(ng/l)	(ng/l)	(ng/l)
Anthracene		0.10		
Fluoranthene		0.80		
Benzo(a)pyrene		0.50		
Benzo(b)fluoranthene		0.40		
Benzo(k)fluoranthene		0.20		
Benzo(b+j+k)fluoranthene*				
Benzo(g,h,i)perylene		0.50		
Indeno(1,2,3-cd)pyrene		1.00		

LOQ SPM***	**LOQ** SPM***	**LOQ** SPM***	**LOQ** SPM***	**LOQ** SPM***
Unit	(ng/l)	(ng/l)	(ng/l)	(ng/l)
Anthracene		0.10		
Fluoranthene		0.80		
Benzo(a)pyrene		0.50		
Benzo(b)fluoranthene		0.40		
Benzo(k)fluoranthene		0.20		
Benzo(b+j+k)fluoranthene*				
Benzo(g,h,i)perylene		0.5		
Indeno(1,2,3-cd)pyrene		1.0		

LOQ Whole Water**	**LOQ** Whole Water**	**LOQ** Whole Water**	**LOQ** Whole Water**	**LOQ** Whole Water**
Unit	(ng/l)	(ng/l)	(ng/l)	(ng/l)
Anthracene	4	0.10	1.1	10
Fluoranthene	11	0.80	9.7	10
Benzo(a)pyrene	2	0.50	0.9	10
Benzo(b)fluoranthene	5	0.40	1.4	10
Benzo(k)fluoranthene	0.7	0.20	1.3	10
Benzo(b+j+k)fluoranthene*				-
Benzo(g,h,i)perylene	6	0.50	1.0	10
Indeno(1,2,3-cd)pyrene	7	1.0	1.5	10

(*): If your chromatographic methoc
(**): LOQ for the method applied fo
(***): Fill the corresponding column

Table 14: Summary of reported PAH Data

Laboratory code	LAB16	LAB17	LAB18	LAB19
LOQ Dissolved***		**LOQ** Dissolved***	**LOQ** Dissolved***	**LOQ** Dissolved***
Unit		(ng/l)	(ng/l)	(ng/l)
Anthracene				
Fluoranthene				
Benzo(a)pyrene				
Benzo(b)fluoranthene				
Benzo(k)fluoranthene				
Benzo(b+j+k)fluoranthene*				
Benzo(g,h,i)perylene				
Indeno(1,2,3-cd)pyrene				

LOQ SPM***		**LOQ** SPM***	**LOQ** SPM***	**LOQ** SPM***
Unit		(ng/l)	(ng/l)	(ng/l)
Anthracene				
Fluoranthene				
Benzo(a)pyrene				
Benzo(b)fluoranthene				
Benzo(k)fluoranthene				
Benzo(b+j+k)fluoranthene*				
Benzo(g,h,i)perylene				
Indeno(1,2,3-cd)pyrene				

LOQ Whole Water**		**LOQ** Whole Water**	**LOQ** Whole Water**	**LOQ** Whole Water**
Unit		(ng/l)	(ng/l)	(ng/l)
Anthracene		2	0.150	<3
Fluoranthene		2	0.100	<3
Benzo(a)pyrene		2	0.150	<3
Benzo(b)fluoranthene		2	0.150	
Benzo(k)fluoranthene		2	0.150	
Benzo(b+j+k)fluoranthene*				<3
Benzo(g,h,i)perylene		2	0.140	<1
Indeno(1,2,3-cd)pyrene		2	0.150	<1

(*): If your chromatographic methoc
(**): LOQ for the method applied fo
(***): Fill the corresponding column

Table 14: Summary of reported PAH Data

Laboratory code	LAB20	LAB21	LAB22
LOQ Dissolved***	**LOQ** Dissolved***	**LOQ** Dissolved***	**LOQ** Dissolved***
Unit	(ng/l)	(ng/l)	(ng/l)
Anthracene			
Fluoranthene			
Benzo(a)pyrene			
Benzo(b)fluoranthene			
Benzo(k)fluoranthene			
Benzo(b+j+k)fluoranthene*			
Benzo(g,h,i)perylene			
Indeno(1,2,3-cd)pyrene			

LOQ SPM***	**LOQ** SPM***	**LOQ** SPM***	**LOQ** SPM***
Unit	(ng/l)	(ng/l)	(ng/l)
Anthracene			
Fluoranthene			
Benzo(a)pyrene			
Benzo(b)fluoranthene			
Benzo(k)fluoranthene			
Benzo(b+j+k)fluoranthene*			
Benzo(g,h,i)perylene			
Indeno(1,2,3-cd)pyrene			

LOQ Whole Water**	**LOQ** Whole Water**	**LOQ** Whole Water**	**LOQ** Whole Water**
Unit	(ng/l)	(ng/l)	(ng/l)
Anthracene	50	1	1
Fluoranthene	50	1	1
Benzo(a)pyrene	10	1	1
Benzo(b)fluoranthene	10	1	1
Benzo(k)fluoranthene	10	1	1
Benzo(b+j+k)fluoranthene*			1
Benzo(g,h,i)perylene	10	1	1
Indeno(1,2,3-cd)pyrene	10	1	1

(*): If your chromatographic methoc
(**): LOQ for the method applied fo
(***): Fill the corresponding column

Table 15: Summary of reported PBDE Data

Laboratory code	LAB1	LAB1	LAB3	LAB4
Standard S1	**Standard S1**		**Standard S1**	**Standard S1**
Unit	(ng/ml)		(ng/ml)	(ng/ml)
Date Received: Date Analysed:	29/12/08 1st vial		22/09/08 06/11/08	19/09/08 19/11/08
BDE-28*	9.10		19.0	17.9
BDE-47*	33.83		87.7	60.9
BDE-99*	50.93		107.9	84.4
BDE-100*	13.96		25.9	20.7
BDE-153*	9.58		18.9	17.9
BDE-154*	9.49		20.4	18.5
BDE-183	n.d.		2.0	
BDE-209	64.68		not determined	
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154	126.89		279.8	220.3

Extract E1	**Extract E1**		**Extract E1**	**Extract E1**
Unit	(ng/ml)		(ng/ml)	(ng/ml)
Date Received: Date Analysed:	03/12/08		22/09/08 10/11/08	19/09/08 19/11/08
BDE-28*	<0.0023		0.4	<0,050
BDE-47*	0.100		0.5	0.073
BDE-99*	0.167		0.7	0.242
BDE-100*	0.033		0.5	0.124
BDE-153*	0.021		0.4	0.077
BDE-154*	0.017		0.3	0.108
BDE-183	0.014		<LOQ	
BDE-209	1.663		not determined	
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154	0.34		3.0	0.624

Table 15: Summary of reported PBDE Data

Laboratory code	LAB5	LAB6	LAB7
Standard S1	**Standard S1**	**Standard S1**	**Standard S1**
Unit	(ng/ml)	(ng/ml)	(ng/ml)
Date Received: Date Analysed:	01/10/08 10/11/08	23/09/08 13/10/08	23/09/2008 15/10/2008
BDE-28*	12	11	12.95
BDE-47*	44	44	49.07
BDE-99*	68	63	73.98
BDE-100*	17	14	18.18
BDE-153*	11	13	13.54
BDE-154*	11	18	12.99
BDE-183	0.5	4	0.31
BDE-209	59	34	94.11
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154		163	180.71

Extract E1	**Extract E1**	**Extract E1**	**Extract E1**
Unit	(ng/ml)	(ng/ml)	(ng/ml)
Date Received: Date Analysed:	01/10/08 10/11/08	23/09/08 13/10/08	23/09/2008 15/10/2008
BDE-28*	< 0.1	<0.1	< 0.08
BDE-47*	0.17	<0.1	0.22
BDE-99*	0.38	0.3	0.62
BDE-100*	<0.1	<0.1	0.15
BDE-153*	0.1	<0.1	0.16
BDE-154*	<0.1	<0.1	0.12
BDE-183	<0.1	<0.1	0.01
BDE-209	10.5	<1	2.82
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154		0.3	1.35

Table 15: Summary of reported PBDE Data

Laboratory code	LAB7	LAB9	LAB10
Standard S1		**Standard S1**	**Standard S1**
Unit		(ng/ml)	(ng/ml)
Date Received: Date Analysed:		23/09/08 29/09/08	 29/11/08
BDE-28*		9.4	7.838
BDE-47*		35.8	36.19
BDE-99*		16.1	58.42
BDE-100*		45.9	13.18
BDE-153*		9.8	8.747
BDE-154*		8.6	8.090
BDE-183			0.297
BDE-209			66.56
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154		125.6	**132.5**

Extract E1		**Extract E1**	**Extract E1**
Unit		(ng/ml)	(ng/ml)
Date Received: Date Analysed:		23/09/08 29/09/08	 21/11/08
BDE-28*	**# # The sum of Total Penta BDE have been obtained using the upper bound approach**	< 5	n.d.
BDE-47*		< 5	0.084
BDE-99*		< 10	0.184
BDE-100*		< 10	0.162
BDE-153*		<10	n.d.
BDE-154*		< 5	n.d.
BDE-183			n.d.
BDE-209			1.292
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154		<10	**0.4**

Table 15: Summary of reported PBDE Data

Laboratory code	LAB11	LAB11	LAB11
Standard S1	**Standard S1**		**Standard S1**
Unit	(ng/ml)		(ng/ml)
Date Received: Date Analysed:	23/09/08 27 - 31/10/2008 **Ion trap: Polaris Q**		23/09/08 27 - 31/10/2008 **High resolution: DFS(Thermo)**
BDE-28* **BDE-47*** **BDE-99*** **BDE-100*** **BDE-153*** **BDE-154*** **BDE-183** **BDE-209**	11 47 62 17 13 14 <1.3 75		11.7 51.1 43.7 13.4 - 13.2 0.48 54.3
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154	164		133.1

Extract E1	**Extract E1**		**Extract E1**
Unit	(ng/ml)		(ng/ml)
Date Received: Date Analysed:	23/09/08 27 - 31/10/2008 **Ion trap: Polaris Q**		23/09/08 27 - 31/10/2008 **High resolution: DFS**
BDE-28* **BDE-47*** **BDE-99*** **BDE-100*** **BDE-153*** **BDE-154*** **BDE-183** **BDE-209**	<1.3 <0.9 <1.7 <4.7 <1.2 <1.4 <1.2 <1.9		0.03 0.10 0.16 0.04 1.51 - 0.03 1.97
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154	<		1.84

Table 15: Summary of reported PBDE Data

Laboratory code	LAB12	LAB12	LAB12	LAB12	LAB12
Standard S1	Standard S1				
Unit	(ng/ml)				
Date Received: Date Analysed:	18.9.2008	3.11.2008	4.11.2008	4.11.2008	4.11.2008
BDE-28*	10.25	7	13	8	13
BDE-47*	38.75	26	46	33	50
BDE-99*	59.5	48	70	51	69
BDE-100*	28.75	24	36	25	30
BDE-153*	30.25	27	39	26	29
BDE-154*	28.75	25	36	25	29
BDE-183					
BDE-209					
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154	196.25				

Extract E1	Extract E1				
Unit	(ng/ml)				
Date Received: Date Analysed:	18.9.2008	3.11.2008	4.11.2008		
BDE-28*	<1	<1.0	<1.0		
BDE-47*	<1	<1.0	<1.0		
BDE-99*	6.15	6	6.3		
BDE-100*	5.3	5.3	5.3		
BDE-153*	<10	<10	<10		
BDE-154*	<10	<10	<10		
BDE-183					
BDE-209					
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154					

Table 15: Summary of reported PBDE Data

Laboratory code	LAB13	LAB14	LAB15
Standard S1	**Standard S1**	**Standard S1**	**Standard S1**
Unit	(ng/ml)	(ng/ml)	(ng/ml)
Date Received: Date Analysed:	22/09/2008 10/01/08	30/09/08 02/12/08	19-Sep 07-Nov
BDE-28*	10	not analysed	16.5
BDE-47*	50	43	47.4
BDE-99*	73	62	19.9
BDE-100*	18	18	75.6
BDE-153*	10	12	12.6
BDE-154*	10	12	13.6
BDE-183	<0.5	not analysed	
BDE-209	135	not analysed	
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154	171		185.6

Extract E1	**Extract E1**	**Extract E1**	**Extract E1**
Unit	(ng/ml)	(ng/ml)	(ng/ml)
Date Received: Date Analysed:	22/09/2008 10/01/08	30/09/08 02/12/08	19-Sep 07-Nov
BDE-28*	<0.5	not analysed	< 0,5
BDE-47*	<0.5	<0.05	< 0,5
BDE-99*	<0.5	<0.05	< 0,5
BDE-100*	<0.5	<0.05	< 0,5
BDE-153*	<0.5	<0.05	< 0,5
BDE-154*	<0.5	<0.05	< 0,5
BDE-183	<0.5	not analysed	
BDE-209	2.9	not analysed	
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154			

Table 15: Summary of reported PBDE Data

Laboratory code	LAB16	LAB17
Standard S1	**Standard S1**	**Standard S1**
Unit	(ng/ml)	(ng/ml)
Date Received: Date Analysed:	18.9.08 21.11.08	22/09/08 28/10/08
BDE-28* **BDE-47*** **BDE-99*** **BDE-100*** **BDE-153*** **BDE-154*** **BDE-183** **BDE-209**	8.2 38.1 52.2 9.5 1.7 2.2 - -	12 43 67 18 12 11 n.b. n.b.
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154	112	163

Extract E1	**Extract E1**	**Extract E1**
Unit	~~(ng/ml)~~ **ng/sample**	(ng/ml)
Date Received: Date Analysed:	18.9.08 21.11.08	22/09/08 28/10/08
BDE-28* **BDE-47*** **BDE-99*** **BDE-100*** **BDE-153*** **BDE-154*** **BDE-183** **BDE-209**	<1 <1 <5 <5 <10 <10	< 5 < 5 < 5 < 5 < 5 < 5 n.b. n.b.
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154	<30	—

Table 15: Summary of reported PBDE Data

Laboratory code	LAB1	LAB1	LAB3	LAB4
Danube dissolved conc.* **	**Danube dissolved conc.*** **		**Danube dissolved conc.*** **	**Danube dissolved conc.*** **
Unit	**(ng/l)**		**(ng/l)**	**(ng/l)**
Date Received: Volume Analysed: Date Analysed:	 29.1 L 03/12/08			
BDE-28*	0.0005			
BDE-47*	0.0148			
BDE-99*	0.0297			
BDE-100*	0.0064			
BDE-153*	0.0018			
BDE-154*	0.0022			
BDE-183	0.0011			
BDE-209	0.1553			
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154	0.06			

Danube SPM conc.* **	**Danube SPM conc.*** **		**Danube SPM conc.*** **	**Danube SPM conc.*** **
Unit	**(ng/l)**		**(ng/l)**	**(ng/l)**
Date Received: Volume Analysed: Date Analysed:	 29.1 L 03/12/08			
BDE-28*	<0.0018			
BDE-47*	0.0096			
BDE-99*	0.0139			
BDE-100*	0.0028			
BDE-153*	0.0025			
BDE-154*	0.0022			
BDE-183	0.0018			
BDE-209	0.1434			
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154	0.03			

Danube whole water conc.	**Danube whole water conc.**	**Danube whole water conc.**	**Danube whole water conc.**	**Danube whole water conc.**
Unit	**(ng/l)**	**(ng/l)**	**(ng/l)**	**(ng/l)**
Date Received: Volume Analysed: Date Analysed:	 29.1 L 03/12/08	 2.3L 29/10/08	22/09/08 0.75 L 11/11/08	19/09/08 1000ml 19/11/08
BDE-28*	0.0005	0.0010	<LOQ	<0,050
BDE-47*	0.0244	0.0238	0.2	0.141
BDE-99*	0.0324	0.0100	0.3	0.205
BDE-100*	0.0203	0.0281	<LOQ	0.065
BDE-153*	0.0039	0.0047	0.4	<0,050
BDE-154*	0.0047	0.0094	0.3	<0,050
BDE-183	0.0029	0.0815	<LOQ	
BDE-209	0.2987	0.6003	not determined	
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154	0.09	0.08	1.2	0.411

Table 15: Summary of reported PBDE Data

Laboratory code	LAB5	LAB6	LAB7
Danube dissolved conc.* **	**Danube dissolved conc.*** **	**Danube dissolved conc.*** **	**Danube dissolved conc.*** **
Unit	**(ng/l)**	**(ng/l)**	**(ng/l)**
Date Received: Volume Analysed: Date Analysed:			
BDE-28* **BDE-47*** **BDE-99*** **BDE-100*** **BDE-153*** **BDE-154*** **BDE-183** **BDE-209**			
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154			

Danube SPM conc.* **	**Danube SPM conc.*** **	**Danube SPM conc.*** **	**Danube SPM conc.*** **
Unit	**(ng/l)**	**(ng/l)**	**(ng/l)**
Date Received: Volume Analysed: Date Analysed:			
BDE-28* **BDE-47*** **BDE-99*** **BDE-100*** **BDE-153*** **BDE-154*** **BDE-183** **BDE-209**			
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154			

Danube whole water conc.	**Danube whole water conc.**	**Danube whole water conc.**	**Danube whole water conc. #**
Unit	**(ng/l)**	**(ng/l)**	**(ng/l)**
Date Received: Volume Analysed: Date Analysed:	22/09/08 not known, outsourced data	19/09/08 2 liters 29/09/08	26/09/2008 1 L 29/09/2008
BDE-28* **BDE-47*** **BDE-99*** **BDE-100*** **BDE-153*** **BDE-154*** **BDE-183** **BDE-209**	< 0.5 < 0.5 < 0.5 < 0.5 < 0.5 < 0.5 * *	<0.25 <0.25 <0.25 <0.25 <0.25 <0.25 <0.25 <2.5	< 0.02 0.04 < 0.01 0.01 < 0.04 < 0.03 < 0.02 0.6
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154	<2.5	<0.25	0.15

Table 15: Summary of reported PBDE Data

Laboratory code	LAB7	LAB9	LAB10
Danube dissolved conc.* **		**Danube dissolved conc.*** **	**Danube dissolved conc.*** **
Unit		**(ng/l)**	**(ng/l)**
Date Received: Volume Analysed: Date Analysed:			
BDE-28* **BDE-47*** **BDE-99*** **BDE-100*** **BDE-153*** **BDE-154*** **BDE-183** **BDE-209**			
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154			

Danube SPM conc.* **		**Danube SPM conc.*** **	**Danube SPM conc.*** **
Unit		**(ng/l)**	**(ng/g) --> (ng/L with TSM 14 mg/L)**
Date Received: Volume Analysed: Date Analysed:			5.0045 g --> 357.5 L 29/11/08
BDE-28* **BDE-47*** **BDE-99*** **BDE-100*** **BDE-153*** **BDE-154*** **BDE-183** **BDE-209**			0.014 --> 0.000191 0.197 --> 0.00276 0.179 --> 0.00252 0.056 --> 0.000791 0.033 --> 0.00046 0.024 --> 0.000336 n.d. 8.717 --> 0.1223
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154			**0.5 --> 0.007**

Danube whole water conc.	**Field blank conc. #**	**Danube whole water conc.**	**Danube whole water conc.**
Unit	**(ng/l)**	**(ng/l)**	**(ng/l)**
Date Received: Volume Analysed: Date Analysed:	26/09/2008 1 L 29/09/2008 **# The values obtained for BDE conc. in the field blank have not been subtracted to the values found for the Danube whole water conc.**	22/09/08 4000 ml 29/09/08	09/10/08
BDE-28* **BDE-47*** **BDE-99*** **BDE-100*** **BDE-153*** **BDE-154*** **BDE-183** **BDE-209**	0.03 0.01 **# # The sum of Total Penta BDE has been obtained using the upper bound approach**	< 10 < 10 < 10 < 10 < 10 < 10	n.d. 0.096 0.011 0.040 0.030 n.d. n.d. n.d.
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154		< 10	**0.2**

Table 15: Summary of reported PBDE Data

Laboratory code	LAB11	LAB11	LAB11
Danube dissolved conc.* **	**Danube dissolved conc.*** **		
Unit	**(ng/l)**		
Date Received: Volume Analysed: Date Analysed:			
BDE-28* **BDE-47*** **BDE-99*** **BDE-100*** **BDE-153*** **BDE-154*** **BDE-183** **BDE-209**			
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154			

Danube SPM conc.* **	**Danube SPM conc.*** **		
Unit	**(ng/l)**		
Date Received: Volume Analysed: Date Analysed:			
BDE-28* **BDE-47*** **BDE-99*** **BDE-100*** **BDE-153*** **BDE-154*** **BDE-183** **BDE-209**			
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154			

Danube whole water conc.	**Danube whole water conc.**		
Unit	**(ng/l)**		
Date Received: Volume Analysed: Date Analysed:	24/09/08 10 liter 27 - 31/10/2008		24/09/08 10 liter 27 - 31/10/2008
	Ion trap: Polaris Q		**High resolution: DFS**
BDE-28*	<0.13	*= LOD*	0.009
BDE-47*	<0.09	*= LOD*	0.044
BDE-99*	<0.17	*= LOD*	0.030
BDE-100*	<0.45	*= LOD*	0.012
BDE-153*	<0.12	*= LOD*	0.014
BDE-154*	<0.14	*= LOD*	0.012
BDE-183	<0.13	*= LOD*	0.021
BDE-209	8	*problems with internal standard*	0.568
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154	<		0.121

Table 15: Summary of reported PBDE Data

Laboratory code	LAB12	LAB12	LAB12	LAB12	LAB12
Danube dissolved conc.* **	Danube dissolved conc.***				
Unit	(ng/l)				
Date Received: Volume Analysed: Date Analysed:	not analysed not analysed not analysed				
BDE-28* **BDE-47*** **BDE-99*** **BDE-100*** **BDE-153*** **BDE-154*** **BDE-183** **BDE-209**	not analysed not analysed not analysed not analysed not analysed not analysed not analysed not analysed				
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154					

Danube SPM conc.* **	Danube SPM conc.***				
Unit	(ng/l)				
Date Received: Volume Analysed: Date Analysed:	not analysed not analysed not analysed				
BDE-28* **BDE-47*** **BDE-99*** **BDE-100*** **BDE-153*** **BDE-154*** **BDE-183** **BDE-209**	not analysed not analysed not analysed not analysed not analysed not analysed not analysed not analysed				
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154					

Danube whole water conc.	Danube whole water conc.				
Unit	(ng/l)				
Date Received: Volume Analysed: Date Analysed:	18.9.2008 100 ml water extracted 22.9.2008, extract analysed 10.10.2008				
BDE-28* **BDE-47*** **BDE-99*** **BDE-100*** **BDE-153*** **BDE-154*** **BDE-183** **BDE-209**	<0.25 <0.25 <0.25 <0.25 not determined (interferences) <1.0				
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154					

Table 15: Summary of reported PBDE Data

Laboratory code	LAB13	LAB14	LAB15
Danube dissolved conc.* **	**Danube dissolved conc.*** **	**Danube dissolved conc.*** **	**Danube dissolved conc.*** **
Unit	**(ng/l)**	**(ng/l)**	**(ng/l)**
Date Received: Volume Analysed: Date Analysed:	22/09/2008 5.5 L 23/09/2008	30/09/08 5 02/12/08	
BDE-28* **BDE-47*** **BDE-99*** **BDE-100*** **BDE-153*** **BDE-154*** **BDE-183** **BDE-209**	0.06 0.10 0.06 <0.05 <0.05 <0.05 <0.05 1.2	not analysed <0.05 <0.05 <0.05 <0.05 <0.05	
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154	0.22		

Danube SPM conc.* **	**Danube SPM conc.*** **	**Danube SPM conc.*** **	**Danube SPM conc.*** **
Unit	**(ng/l)**	**(ng/l)**	**(ng/l)**
Date Received: Volume Analysed: Date Analysed:	22/09/2008 5.5 L 23/09/2008	30/09/08 5 02/12/08	
BDE-28* **BDE-47*** **BDE-99*** **BDE-100*** **BDE-153*** **BDE-154*** **BDE-183** **BDE-209**	<0.01 0.03 0.02 <0.01 <0.01 <0.01 1.8	not analysed <0.05 <0.05 <0.05 <0.05 <0.05	
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154	0.05		

Danube whole water conc.	**Danube whole water conc.**	**Danube whole water conc.**	**Danube whole water conc.**
Unit	**(ng/l)**	**(ng/l)**	**(ng/l)**
Date Received: Volume Analysed: Date Analysed:	22/09/2008 5.5 L 23/09/2008	30/09/08 5 02/12/08	19-Sep 1 liter 07-Nov
BDE-28* **BDE-47*** **BDE-99*** **BDE-100*** **BDE-153*** **BDE-154*** **BDE-183** **BDE-209**	0.06 0.13 0.08 <0.05 <0.05 <0.05 <0.05 3.0	not analysed <0.05 <0.05 <0.05 <0.05 <0.05	0.72 < 0,5 < 0,5 < 0,5 < 0,5 < 0,5
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154	0.27		

Table 15: Summary of reported PBDE Data

Laboratory code	LAB16	LAB17
Danube dissolved conc.* **	**Danube dissolved conc.*** **	**Danube dissolved conc.*** **
Unit	**(ng/l)**	**(ng/l)**
Date Received: Volume Analysed: Date Analysed:		
BDE-28* **BDE-47*** **BDE-99*** **BDE-100*** **BDE-153*** **BDE-154*** **BDE-183** **BDE-209**		
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154		

Danube SPM conc.* **	**Danube SPM conc.*** **	**Danube SPM conc.*** **
Unit	**(ng/l)**	**(ng/l)**
Date Received: Volume Analysed: Date Analysed:		
BDE-28* **BDE-47*** **BDE-99*** **BDE-100*** **BDE-153*** **BDE-154*** **BDE-183** **BDE-209**		
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154		

Danube whole water conc.	**Danube whole water conc.**	**Danube whole water conc.**
Unit	**(ng/l)**	**(ng/l)**
Date Received: Volume Analysed: Date Analysed:	18.9.08 1000 ml	22/09/08 28/10/08 28/10/08
BDE-28* **BDE-47*** **BDE-99*** **BDE-100*** **BDE-153*** **BDE-154*** **BDE-183** **BDE-209**	<1 <1 <5 <5 <10 <10	< 5 < 5 < 5 < 5 < 5 < 5 n.b. n.b.
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154		—

Table 15: Summary of reported PBDE Data

Laboratory code	LAB1	LAB1	LAB3	LAB4
LOQ Dissolved***	**LOQ** Dissolved***		**LOQ** Dissolved***	**LOQ** Dissolved***
Unit	**(ng/l)**		**(ng/l)**	**(ng/l)**
BDE-28*				
BDE-47*				
BDE-99*				
BDE-100*				
BDE-153*				
BDE-154*				
BDE-183				
BDE-209				
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154				

LOQ SPM***	**LOQ** SPM***		**LOQ** SPM***	**LOQ** SPM***
Unit	**(ng/l)**		**(ng/l)**	**(ng/l)**
BDE-28*				
BDE-47*				
BDE-99*				
BDE-100*				
BDE-153*				
BDE-154*				
BDE-183				
BDE-209				
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154				

LOQ Whole water**	**LOQ** Whole water**	**LOQ** Whole water**	**LOQ** Whole water**	**LOQ** Whole water**
Unit	**(ng/l)**	**(ng/l)**	**(ng/l)**	**(ng/l)**
BDE-28*	0.0005	0.0005	0.2	0.050
BDE-47*	0.002	0.002	0.2	0.050
BDE-99*	0.002	0.002	0.2	0.050
BDE-100*	0.002	0.002	0.2	0.050
BDE-153*	0.002	0.002	0.2	0.050
BDE-154*	0.002	0.002	0.2	0.050
BDE-183	0.002	0.002	0.2	
BDE-209	0.01	0.01		
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154				

(*): compulsory
(**): LOQ for the method applied for water analysis.
(***): Fill the corresponding column if fractions have been analysed separately

Table 15: Summary of reported PBDE Data

Laboratory code	LAB5	LAB6	LAB7
LOQ Dissolved***	**LOQ** Dissolved***	**LOQ** Dissolved***	**LOQ** Dissolved***
Unit	**(ng/l)**	**(ng/l)**	**(ng/l)**
BDE-28*			
BDE-47*			
BDE-99*			
BDE-100*			
BDE-153*			
BDE-154*			
BDE-183			
BDE-209			
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154			

LOQ SPM***	**LOQ** SPM***	**LOQ** SPM***	**LOQ** SPM***
Unit	**(ng/l)**	**(ng/l)**	**(ng/l)**
BDE-28*			
BDE-47*			
BDE-99*			
BDE-100*			
BDE-153*			
BDE-154*			
BDE-183			
BDE-209			
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154			

LOQ Whole water**	**LOQ** Whole water**	**LOQ** Whole water**	**LOQ** Whole water**
Unit	**(ng/l)**	**(ng/l)**	**(ng/l)**
BDE-28*	0.5	<0.25	0.02
BDE-47*	0.5	<0.25	0.01
BDE-99*	0.5	<0.25	0.01
BDE-100*	0.5	<0.25	0.01
BDE-153*	0.5	<0.25	0.04
BDE-154*	0.5	<0.25	0.03
BDE-183	*	<0.25	0.02
BDE-209	*	<2.5	0.57
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154	<2.5	<0.25	0.12

(*): compulsory
(**): LOQ for the method applied for water analysis.
(***): Fill the corresponding column if fractions have been analysed separately

Table 15: Summary of reported PBDE Data

Laboratory code	LAB7	LAB9	LAB10
LOQ Dissolved*** **		**LOQ** Dissolved*** **	**LOQ** Dissolved*** **
Unit		**(ng/l)**	**(ng/l)**
BDE-28*			
BDE-47*			
BDE-99*			
BDE-100*			
BDE-153*			
BDE-154*			
BDE-183			
BDE-209			
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154			

LOQ SPM*** **		**LOQ** SPM*** **	**LOQ** SPM*** **
Unit		**(ng/l)**	**(ng/l)**
BDE-28*			
BDE-47*			
BDE-99*			
BDE-100*			
BDE-153*			
BDE-154*			
BDE-183			
BDE-209			
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154			

LOQ Whole water**		**LOQ** Whole water**	**LOQ** Whole water**
Unit		**(ng/l)**	**(ng/l)**
BDE-28*		< 10	
BDE-47*		< 10	
BDE-99*		< 10	
BDE-100*		< 10	
BDE-153*		< 10	
BDE-154*		< 10	
BDE-183			
BDE-209			
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154		< 10	

(*): compulsory
(**): LOQ for the method applied for water analysis.
(***): Fill the corresponding column if fractions have been analysed separately

Table 15: Summary of reported PBDE Data

Laboratory code	LAB11	LAB11	LAB11
LOQ Dissolved*** **	**LOQ** Dissolved*** **		
Unit	**(ng/l)**		
BDE-28*			
BDE-47*			
BDE-99*			
BDE-100*			
BDE-153*			
BDE-154*			
BDE-183			
BDE-209			
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154			

LOQ SPM*** **	**LOQ** SPM*** **		
Unit	**(ng/l)**		
BDE-28*			
BDE-47*			
BDE-99*			
BDE-100*			
BDE-153*			
BDE-154*			
BDE-183			
BDE-209			
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154			

	Ion trap: Polaris Q		**High resolution: DFS**
LOQ Whole water**	**LOQ** Whole water**		**LOQ** Whole water**
Unit	**(ng/l)**		**(ng/l)**
BDE-28*	0.4		± 0.01
BDE-47*	0.3		± 0.01
BDE-99*	0.5		± 0.01
BDE-100*	1.4		± 0.01
BDE-153*	0.4		± 0.01
BDE-154*	0.4		± 0.01
BDE-183	0.4		± 0.01
BDE-209	0.6		± 0.10
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154			

(*): compulsory
(**): LOQ for the method applied for water analysis.
(***): Fill the corresponding column if fractions have been analysed separately

Table 15: Summary of reported PBDE Data

Laboratory code	LAB12	LAB12	LAB12	LAB12	LAB12
LOQ Dissolved*** **	LOQ** Dissolved***				
Unit	(ng/l)				
BDE-28*	not determined				
BDE-47*	not determined				
BDE-99*	not determined				
BDE-100*	not determined				
BDE-153*	not determined				
BDE-154*	not determined				
BDE-183					
BDE-209					
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154					

LOQ SPM*** **	LOQ** SPM***				
Unit	(ng/l)				
BDE-28*	not determined				
BDE-47*	not determined				
BDE-99*	not determined				
BDE-100*	not determined				
BDE-153*	not determined				
BDE-154*	not determined				
BDE-183					
BDE-209					
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154					

LOQ Whole water**	LOQ** Whole water				
Unit	(ng/l)				
BDE-28*	0.25				
BDE-47*	0.25				
BDE-99*	0.25				
BDE-100*	0.25				
BDE-153*	not determined				
BDE-154*	1				
BDE-183					
BDE-209					
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154					

(*): compulsory
(**): LOQ for the method applied for water analysis.
(***): Fill the corresponding column if fractions have been analysed separately

Table 15: Summary of reported PBDE Data

Laboratory code	LAB13	LAB14	LAB15
LOQ Dissolved***	**LOQ** Dissolved***	**LOQ** Dissolved***	**LOQ** Dissolved***
Unit	**(ng/l)**	**(ng/l)**	**(ng/l)**
BDE-28*	<0.05	not analysed	
BDE-47*	<0.05	<0.05	
BDE-99*	<0.05	<0.05	
BDE-100*	<0.05	<0.05	
BDE-153*	<0.05	<0.05	
BDE-154*	<0.05	<0.05	
BDE-183	<0.05		
BDE-209	<0.5		
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154			

LOQ SPM***	**LOQ** SPM***	**LOQ** SPM***	**LOQ** SPM***
Unit	**(ng/l)**	**(ng/l)**	**(ng/l)**
BDE-28*	<0.01	not analysed	
BDE-47*	<0.01	<0.05	
BDE-99*	<0.01	<0.05	
BDE-100*	<0.01	<0.05	
BDE-153*	<0.01	<0.05	
BDE-154*	<0.01	<0.05	
BDE-183	<0.01		
BDE-209	<0.05		
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154			

LOQ Whole water**	**LOQ** Whole water**	**LOQ** Whole water**	**LOQ** Whole water**
Unit	**(ng/l)**	**(ng/l)**	**(ng/l)**
BDE-28*	<0.05	not analysed	0.5
BDE-47*	<0.05	<0.05	0.5
BDE-99*	<0.05	<0.05	0.5
BDE-100*	<0.05	<0.05	0.5
BDE-153*	<0.05	<0.05	0.5
BDE-154*	<0.05	<0.05	0.5
BDE-183	<0.05		
BDE-209	<0.5		
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154			3

(*): compulsory
(**): LOQ for the method applied for water analysis.
(***): Fill the corresponding column if fractions have been analysed separately

Table 15: Summary of reported PBDE Data

Laboratory code	LAB16	LAB17
LOQ Dissolved***	**LOQ** Dissolved***	**LOQ** Dissolved***
Unit	**(ng/l)**	**(ng/l)**
BDE-28*		
BDE-47*		
BDE-99*		
BDE-100*		
BDE-153*		
BDE-154*		
BDE-183		
BDE-209		
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154		

LOQ SPM***	**LOQ** SPM***	**LOQ** SPM***
Unit	**(ng/l)**	**(ng/l)**
BDE-28*		
BDE-47*		
BDE-99*		
BDE-100*		
BDE-153*		
BDE-154*		
BDE-183		
BDE-209		
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154		

LOQ Whole water**	**LOQ** Whole water**	**LOQ** Whole water**
Unit	**(ng/l)**	**(ng/l)**
BDE-28*	1	5
BDE-47*	1	5
BDE-99*	5	5
BDE-100*	5	5
BDE-153*	10	5
BDE-154*	10	5
BDE-183	-	n.b.
BDE-209	-	n.b.
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154	30	

(*): compulsory
(**): LOQ for the method applied for water analysis.
(***): Fill the corresponding column if fractions have been analysed separately

Table 16: Summary of reported Alkylphenol Data

Laboratory code	LAB2	LAB3	LAB4
Standard S3	**Standard S3**	**Standard S3**	**Standard S3**
Unit	(ng/ml)	(ng/ml)	(ng/ml)
Date Received:	22/09/08	29/09/08	19/09/08
Date Analysed:	12/11/08	09/12/08	30/09/08
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].	489.4	654	673
4-tert-octylphenol (OP) [CAS no. 140-66-9]	230.7	435	398
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]			
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].			

Extract E2	**Extract E2**	**Extract E2**	**Extract E2**
Unit	(ng/ml)	(ng/ml)	(ng/ml)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].	286.7	1065	363
4-tert-octylphenol (OP) [CAS no. 140-66-9]	15.8	24	30
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]			
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].			

Danube dissolved conc.**	**Danube dissolved conc.****	**Danube dissolved conc.****	**Danube dissolved conc.****
Unit	(ng/l)	(ng/l)	(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].			
4-tert-octylphenol (OP) [CAS no. 140-66-9]			
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]			
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].			

Danube SPM conc.**	**Danube SPM conc.****	**Danube SPM conc.****	**Danube SPM conc.****
Unit	(ng/l)	(ng/l)	(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].			
4-tert-octylphenol (OP) [CAS no. 140-66-9]			
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]			
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].			

Danube whole water conc.	**Danube whole water conc.**	**Danube whole water conc.**	**Danube whole water conc.**
Unit	(ng/l)	(ng/l)	(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].	< LQ	<100	20
4-tert-octylphenol (OP) [CAS no. 140-66-9]	< LQ	<10	<5
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]			
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].			

LOQ* dissolved	**LOQ* dissolved**	**LOQ* dissolved**	**LOQ* dissolved**
Unit	(ng/l)	(ng/l)	(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].			
4-tert-octylphenol (OP) [CAS no. 140-66-9]			
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]			
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].			

LOQ* SPM	**LOQ* SPM**	**LOQ* SPM**	**LOQ* SPM**
Unit	(ng/l)	(ng/l)	(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].			
4-tert-octylphenol (OP) [CAS no. 140-66-9]			
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]			
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].			

LOQ* whole water	**LOQ* whole water**	**LOQ* whole water**	**LOQ* whole water**
Unit	(ng/l)	(ng/l)	(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].	0.030	100	<20
4-tert-octylphenol (OP) [CAS no. 140-66-9]	0.015	10	<5
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]			
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].			

(*): LOQ for the method applied for water
(**): Fill the corresponding column if fractions have been analysed separately

Table 16: Summary of reported Alkylphenol Data

Laboratory code	LAB4	LAB5	LAB6
Standard S3	**Standard S3**	**Standard S3**	**Standard S3**
Unit	(ng/ml)	(ng/ml)	(ng/ml)
Date Received:	19/09/08	01/10/08	23/09/08
Date Analysed:	19/11/08	10/11/08	13/10/08
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].	51.4		640
4-tert-octylphenol (OP) [CAS no. 140-66-9]	60.8	55	428
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]	107		
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].	80.8		

Extract E2	**Extract E2**	**Extract E2**	**Extract E2**
Unit	(ng/ml)	(ng/ml)	(ng/ml)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].	25.1	20	222
4-tert-octylphenol (OP) [CAS no. 140-66-9]	<25	350	<25
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]	655		
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].	353		

Danube dissolved conc.**	**Danube dissolved conc.****	**Danube dissolved conc.****	**Danube dissolved conc.****
Unit	(ng/l)	(ng/l)	(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].			
4-tert-octylphenol (OP) [CAS no. 140-66-9]			
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]			
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].			

Danube SPM conc.**	**Danube SPM conc.****	**Danube SPM conc.****	**Danube SPM conc.****
Unit	(ng/l)	(ng/l)	(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].			
4-tert-octylphenol (OP) [CAS no. 140-66-9]			
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]			
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].			

Danube whole water conc.	**Danube whole water conc.**	**Danube whole water conc.**	**Danube whole water conc.**
Unit	(ng/l)	(ng/l)	(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].	27.1	<100	<50
4-tert-octylphenol (OP) [CAS no. 140-66-9]	<5	<5	<4
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]	83.9		
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].	198		

LOQ* dissolved	**LOQ* dissolved**	**LOQ* dissolved**	**LOQ* dissolved**
Unit	(ng/l)	(ng/l)	(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].			
4-tert-octylphenol (OP) [CAS no. 140-66-9]			
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]			
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].			

LOQ* SPM	**LOQ* SPM**	**LOQ* SPM**	**LOQ* SPM**
Unit	(ng/l)	(ng/l)	(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].			
4-tert-octylphenol (OP) [CAS no. 140-66-9]			
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]			
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].			

LOQ* whole water	**LOQ* whole water**	**LOQ* whole water**	**LOQ* whole water**
Unit	(ng/l)	(ng/l)	(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].	<25,0	100	<50
4-tert-octylphenol (OP) [CAS no. 140-66-9]	<5,0	5	<12
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]	<25		
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].	<25		

(*): LOQ for the method applied for water
(**): Fill the corresponding column if fractions have been analysed separately

Table 16: Summary of reported Alkylphenol Data

Laboratory code	LAB7	LAB7	LAB9
Standard S3	**Standard S3**		**Standard S3**
Unit	(ng/ml)		(ng/ml)
Date Received: Date Analysed:	23/09/2008 10/09/08		23/09/08 26/09/08
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3]. 4-tert-octylphenol (OP) [CAS no. 140-66-9] 4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3] 4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].	507 766.2 785.5 386.1		671 320

Extract E2	**Extract E2**		**Extract E2**
Unit	(ng/ml)		(ng/ml)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3]. 4-tert-octylphenol (OP) [CAS no. 140-66-9] 4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3] 4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].	218.3 46.8 276.1 214.9		387 25

Danube dissolved conc.**	**Danube dissolved conc.****		**Danube dissolved conc.****
Unit	(ng/l)		(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3]. 4-tert-octylphenol (OP) [CAS no. 140-66-9] 4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3] 4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].			

Danube SPM conc.**	**Danube SPM conc.****		**Danube SPM conc.****
Unit	(ng/l)		(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3]. 4-tert-octylphenol (OP) [CAS no. 140-66-9] 4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3] 4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].			

Danube whole water conc.	**Danube whole water conc. #**	**Field blank conc. #**	**Danube whole water conc.**
Unit	(ng/l)	(ng/l)	(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3]. 4-tert-octylphenol (OP) [CAS no. 140-66-9] 4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3] 4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].	20.3 2.9 9.5 < 50	11.9 2.3 5.4 # The values obtained for Alkylphenol conc. in the field blank have not been subtracted to the values found for the Danube whole water conc.	< 20 < 20

LOQ* dissolved	**LOQ* dissolved**	**LOQ* dissolved**	**LOQ* dissolved**
Unit	(ng/l)		(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3]. 4-tert-octylphenol (OP) [CAS no. 140-66-9] 4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3] 4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].			

LOQ* SPM	**LOQ* SPM**	**LOQ* SPM**	**LOQ* SPM**
Unit	(ng/l)		(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3]. 4-tert-octylphenol (OP) [CAS no. 140-66-9] 4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3] 4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].			

LOQ* whole water	**LOQ* whole water**	**LOQ* whole water**	**LOQ* whole water**
Unit	(ng/l)		(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3]. 4-tert-octylphenol (OP) [CAS no. 140-66-9] 4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3] 4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].	1 1 4 50		< 20 < 20

(*): LOQ for the method applied for water
(**): Fill the corresponding column if fractions have been analysed separately

Table 16: Summary of reported Alkylphenol Data

Laboratory code	LAB10	LAB11	LAB12
Standard S3	**Standard S3**	**Standard S3**	**Standard S3**
Unit	(ng/ml)	(ng/ml)	(ng/ml)
Date Received: Date Analysed:	13/11/08 27/11/08	23/09/08 28/10/08	19.9.2008
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].	750	552	915.5
4-tert-octylphenol (OP) [CAS no. 140-66-9]	250	432	387
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]			not determined
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].			not determined

Extract E2	**Extract E2**	**Extract E2**	**Extract E2**
Unit	(ng/ml)	(ng/ml)	(ng/ml)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].	440	320	464
4-tert-octylphenol (OP) [CAS no. 140-66-9]	44	28	21.5
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]			not determined
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].			not determined

Danube dissolved conc.**	**Danube dissolved conc.****	**Danube dissolved conc.****	**Danube dissolved conc.****
Unit	(ng/l)	(ng/l)	(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].	330		not determined
4-tert-octylphenol (OP) [CAS no. 140-66-9]	< 5		not determined
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]			not determined
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].			not determined

Danube SPM conc.**	**Danube SPM conc.****	**Danube SPM conc.****	**Danube SPM conc.****
Unit	(ng/g)	(ng/l)	(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].	29		not determined
4-tert-octylphenol (OP) [CAS no. 140-66-9]	< 5		not determined
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]			not determined
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].			not determined

Danube whole water conc.	**Danube whole water conc.**	**Danube whole water conc.**	**Danube whole water conc.**
Unit	(ng/l)	(ng/l)	(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].		100	<100
4-tert-octylphenol (OP) [CAS no. 140-66-9]		<50	<50
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]			<100
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].			not determined

LOQ* dissolved	**LOQ* dissolved**	**LOQ* dissolved**	**LOQ* dissolved**
Unit	(ng/l)	(ng/l)	(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].	25		not determined
4-tert-octylphenol (OP) [CAS no. 140-66-9]	5		not determined
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]			not determined
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].			not determined

LOQ* SPM	**LOQ* SPM**	**LOQ* SPM**	**LOQ* SPM**
Unit	(ng/g)	(ng/l)	(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].	25		not determined
4-tert-octylphenol (OP) [CAS no. 140-66-9]	5		not determined
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]			not determined
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].			not determined

LOQ* whole water	**LOQ* whole water**	**LOQ* whole water**	**LOQ* whole water**
Unit	(ng/l)	(ng/l)	(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].		150	100
4-tert-octylphenol (OP) [CAS no. 140-66-9]		150	50
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]			100
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].			not determined

(*): LOQ for the method applied for water
(**): Fill the corresponding column if fractions have been analysed separately

Table 16: Summary of reported Alkylphenol Data

Laboratory code	LAB13	LAB14
Standard S3	**Standard S3**	**Standard S3**
Unit	(ng/ml)	(ng/ml)
Date Received: Date Analysed:	18-Sep 07-Oct	22/09/08 20/11/08
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].	625	580
4-tert-octylphenol (OP) [CAS no. 140-66-9]	419	410
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]	683	
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].	357	

Extract E2	**Extract E2**	**Extract E2**
Unit	(ng/ml)	(ng/ml)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].	370	450
4-tert-octylphenol (OP) [CAS no. 140-66-9]	<LOQ	38
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]	480	
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].	400	

should be corrected for blank value from exctraction procedure

Danube dissolved conc.**	**Danube dissolved conc.****	**Danube dissolved conc.****
Unit	(ng/l)	(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].	50	
4-tert-octylphenol (OP) [CAS no. 140-66-9]	<LOQ	
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]	55	
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].	14	

Danube SPM conc.**	**Danube SPM conc.****	**Danube SPM conc.****
Unit	(ng/l)	(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].	BLANK	
4-tert-octylphenol (OP) [CAS no. 140-66-9]	<LOQ	
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]	BLANK	
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].	BLANK	

Danube whole water conc.	**Danube whole water conc.**	**Danube whole water conc.**
Unit	(ng/l)	(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].	50	<44
4-tert-octylphenol (OP) [CAS no. 140-66-9]	<LOQ	<3,2
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]	55	
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].	14	

LOQ* dissolved	**LOQ* dissolved**	**LOQ* dissolved**
Unit	(ng/l)	(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].	30	
4-tert-octylphenol (OP) [CAS no. 140-66-9]	5	
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]	30	
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].	15	

LOQ* SPM	**LOQ* SPM**	**LOQ* SPM**
Unit	(ng/l)	(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].	50	
4-tert-octylphenol (OP) [CAS no. 140-66-9]	5	
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]	50	
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].	15	

LOQ* whole water	**LOQ* whole water**	**LOQ* whole water**
Unit	(ng/l)	(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].		<44
4-tert-octylphenol (OP) [CAS no. 140-66-9]		<3,2
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]		
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].		

(*): LOQ for the method applied for water
(**): Fill the corresponding column if fractions have been analysed separately

Table 16: Summary of reported Alkylphenol Data

Laboratory code	LAB15	LAB16	LAB17
Standard S3	**Standard S3**	**Standard S3**	**Standard S3**
Unit	(ng/ml)	~~(ng/ml)~~ **ng/sample**	(ng/ml)
Date Received:	19-Sep	18.9.08	22/09/08
Date Analysed:	25-Sep	18.10.08	24/09/08
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].	539	278	540
4-tert-octylphenol (OP) [CAS no. 140-66-9]	381	451	200
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]		-	
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].		-	

Extract E2	**Extract E2**	**Extract E2**	**Extract E2**
Unit	(ng/ml)	~~(ng/ml)~~ **ng/sample**	(ng/ml)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].	215	96	310
4-tert-octylphenol (OP) [CAS no. 140-66-9]	32	20	25
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]		-	
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].		-	

Danube dissolved conc.**	**Danube dissolved conc.****	**Danube dissolved conc.****	**Danube dissolved conc.****
Unit	(ng/l)	(ng/l)	(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].			
4-tert-octylphenol (OP) [CAS no. 140-66-9]			
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]			
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].			

Danube SPM conc.**	**Danube SPM conc.****	**Danube SPM conc.****	**Danube SPM conc.****
Unit	(ng/l)	(ng/l)	(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].			
4-tert-octylphenol (OP) [CAS no. 140-66-9]			
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]			
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].			

Danube whole water conc.	**Danube whole water conc.**	**Danube whole water conc.**	**Danube whole water conc.**
Unit	(ng/l)	(ng/l)	(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].	15	22	< 10
4-tert-octylphenol (OP) [CAS no. 140-66-9]	2	2.5	< 6
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]		-	
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].		-	

LOQ* dissolved	**LOQ* dissolved**	**LOQ* dissolved**	**LOQ* dissolved**
Unit	(ng/l)	(ng/l)	(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].			
4-tert-octylphenol (OP) [CAS no. 140-66-9]			
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]			
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].			

LOQ* SPM	**LOQ* SPM**	**LOQ* SPM**	**LOQ* SPM**
Unit	(ng/l)	(ng/l)	(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].			
4-tert-octylphenol (OP) [CAS no. 140-66-9]			
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]			
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].			

LOQ* whole water	**LOQ* whole water**	**LOQ* whole water**	**LOQ* whole water**
Unit	(ng/l)	(ng/l)	(ng/l)
4-nonylphenols (NP) –mixture of isomers [CAS no. 84852-15-3].	29	1	10
4-tert-octylphenol (OP) [CAS no. 140-66-9]	31	1	6
4-nonylphenol monoethoxylates (NP1EO) – mixture of isomers [CAS no. 26027-38-3]			
4-nonylphenol diethoxylates (NP2EO) – mixture of isomers [CAS no. 26027-38-2].			

(*): LOQ for the method applied for water
(**): Fill the corresponding column if fractions have been analysed separately

Annex III

Certificates of PAH and PBDE standard solutions

GRAVIMETRIC CERTIFICATE

General Product Data:

Product Name: PAH Standard solution
Product No.: S-4544-ASS-NO

Batch Specific Data:

Batch No.: 7682

Product description:

Compound	Prod.no.	CAS no.	Batch no.	Purity	Grav. conc.
Anthracene	1049.14	120-12-7	1759	97.8 %	20 ng/ml
Fluroanthene	0260.16	206-44-0	1725	99.6 %	80 ng/ml
Benzo[a]pyrene	0239.20	50-32-8	3668	98.3 %	40 ng/ml
Benzo[b]fluoranthene	0263.20	205-99-2	7554	99.9 %	50 ng/ml
Benzo[k]fluoranthene	0265.20	207-08-9	5634	99.7 %	50 ng/ml
Benzo[ghi]perylene	0222.22	191-24-2	7605	99.1 %	40 ng/ml
Indeno[1,2,3-cd]pyrene	0277.22	193-39-5	7606	99.6 %	40 ng/ml

The gravimetric concentrations have not been adjusted for compound impurities.

Solvent: n-Nonane, Prod. Nr 1245.9, Batch 2189
Purity: 99.2 %
Density: 0.71 g/mL

Tolerance: The uncertainty in the preparation of this standard is less than ± 5 %

Quantity: 1.2 mL

Storage: Dark and cool
Before opening allow standard to reach room temperature

Expiry date: Guaranteed 1 year from date of issue

Trondheim, 15 September 2008

Issued by: Approved by:

Maria Haugnæss Inge Fenstad

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GRAVIMETRIC CERTIFICATE

General Product Data:
Product Name: PBDE Standard solution
Product No.: S-4545-ASS-T

Batch Specific Data:
Batch No.: 7686

Product description:

Compound	Prod.no.	CAS no.	Batch no.	Purity	Grav. conc.
Tribromodiphenyl ether PBDE-28	1961.12	41318-75-6	3515	99.0 %	10 ng/ml
2,2',4,4'-Tetrabromodiphenyl ether PBDE-47	1962.12	5436-43-1	3960	99.7 %	40 ng/ml
2,2',4,4',5-Pentabromodiphenyl ether PBDE-99	1967.12	60348-60-9	7316	99.9 %	60 ng/ml
2,2',4,4',6-Pentabromodiphenyl ether PBDE-100	1968.12	189084-64-8	4268	99.4 %	15 ng/ml
2,2',4,4',5,5'-Hexabromodiphenyl ether PBDE-153	1971.12	68631-49-2	4223	98.0 %	10 ng/ml
2,2',4,4',5,6'-Hexabromodiphenyl ether PBDE-154	1972.12	207122-15-4	4360	98.8 %	10 ng/ml
Decabromodiphenyl ether PBDE-209	1811.12	1163-19-5	3863	> 99 %	100 ng/ml

The gravimetric concentrations have not been adjusted for compound impurities.

Solvent: Toluene, Ultra resi-analyzed, Batch 0713400009
Purity: 99.8 %
Density: 0.8667 g/mL

Tolerance: The uncertainty in the preparation of this standard is less than ± 5 %

Quantity: 1.1 mL

Storage: Dark and cool
Before opening allow standard to reach room temperature

Expiry date: Guaranteed 1 year from date of issue

Trondheim, 15 September 2008

Issued by: Approved by:

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Annex IV

CMA on-site 2 Workshop Agenda

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre
Institute for Environment and Sustainability
Rural, Water and Ecosystem Resources

11.9.08

2ND TECHNICAL ON-SITE WORKSHOP

ON

WFD CHEMICAL MONITORING

JRC IES RWER, ICPDR,

HUNGARIAN MINISTRY OF ENVIRONMENT AND WATER

BUDAPEST

HUNGARY
17./ 18. SEPTEMBER 2008

FINAL DRAFT AGENDA

Workshop venue:
Hungarian Ministry of Environment and Water
1011 Budapest Fő utca 44-50. (5 minutes from the METRO 2nd line station at Batthyany square)
Conference Room, Building "A", 7th floor

Wednesday, 17.9.2008

Item	*Time*	*Issue*
(1)	**10:00**	**WELCOME** *Mr. Gyula HOLLÓ, Head of the Department of River Basin Management and Water Protection, Hungarian Water Director*
(2)	**10:15**	**INTRODUCTION TO WORKSHOP SCOPE AND ORGANISATION** *Georg Hanke, JRC IES RWER*
(3)	**10:30**	**ROUND TABLE - PRESENTATION OF PARTICIPANTS**

Item	*Time*	*Issue*
		ALL
(4)	**10:45**	**HAZARDOUS SUBSTANCES IN THE CONTEXT OF RISK ASSESSMENT IN THE DANUBE RIVER BASIN** *Jaroslav Slobodnik, EnvironmentalInstitute*
	11:15	***Coffee Break***
(5)	**11:30**	**WATER FRAMEWORK DIRECTIVE – STATE OF THE EQS DIRECTIVE - CMA** *Mario Carere, Istituto Superiore di Sanità Italy (Dipartimento Ambiente), CMA chair*
(6)	**12:00**	**GUIDANCE FOR CHEMICAL MONITORING – STATE OF THE DOCUMENTS** *Georg Hanke, Mario Carere, Stefano Polesello JRC IES RWER, ISS, IRSA*
	12:30	***Lunch Break*** A'la Karte Kisvendéglö, 1011 Budapest, Iskola u.29
(7)	**14:00**	**CMA on-site 1** *Georg Hanke RWER*
(8)	**14:30**	**Water analysis for WFD - partitioning and "whole water"** Stefano Polesello, IRSA
	15:00	***Coffee Break***
(9)	**15:30**	**ANALYSIS OF WFD PRORITY POLLUTANTS IN WATER** Presentation and discussion of approaches ▪ PAH ▪ PBDE ▪ Alkylphenols *CMA on-site team + participants*
(10)	**16:30**	**BRIEFING FOR SAMPLING AND LOGISTICAL QUESTIONS** *CMA on-site team*
	17:00	*End*
	20:00	**Workshop Dinner at Restaurant Rozmaring Kertvendéglő** Árpád fejedelem útja 125, 1036 Budapest) ca. 10 minutes from the Ministry. Take the electric train "HÉV" from Batthyány tér till the 3rd stop "Tímár utca". Travel takes 7 minutes)

Thursday, 18.9.08

Item	*Time*	*Issue*
(11)	**8:00**	**MEETING AT QUAY "Batthyányi tér" TO BOARD ARGUS AND LEANYFALU**
		ALL
(12)	**8:30**	**FIELD SAMPLING**
		AND
		SAMPLE PREPARATION
		CMA on-site Teams
	13:00	***Snack***
	14:00	**Arrival at Budapest "Batthyányi tér"**
	14:30	*END*

European Commission

EUR 24081 EN – Joint Research Centre – Institute for Environment and Sustainability
Title: Comparison of Monitoring Approaches for Selected Priority Pollutants in Surface Water CMA on-site 2
Author(s): Georg Hanke, Jan Wollgast, Giulio Mariani, Tania Huber, Helle Skejø, Giovanni Locoro, Serafino Contini and Giovanni Bidoglio
Luxembourg: Office for Official Publications of the European Communities
2009 – 141 pp. – 29.7 x 21 cm
EUR – Scientific and Technical Research series – ISSN 1018-5593
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DOI 10.2788/46024

Abstract
27 Analytical Laboratories from eleven EU Member States and two non-EU countries have participated in a technical on-site event during which sampling and analytical methodologies for chemical monitoring according to proposed WFD provisions have been compared. Coordination of the project was provided by the European Commission Joint Research Centre in collaboration with the Italian Water Research Institute, the Hungarian Ministry of Environment and the Serbian Ministry for Environment and Spatial Planning. The Laboratories had been invited to take samples from a major European river according to their standard protocols and to analyse them for PAHs, PBDE and Nonyl-, Octylphenol.
It was shown that even some of the most challenging WFD priority substances, selected on purpose for this exercise, can be measured at WFD relevant concentrations (0.3 x EQS) with methods currently applied in Member States. Depending on the analyte group, the obtained results were not within proposed data quality limits for some participants and therefore further development of methods and harmonisations of efforts is suggested.

The mission of the JRC is to provide customer-driven scientific and technical support for the conception, development, implementation and monitoring of EU policies. As a service of the European Commission, the JRC functions as a reference centre of science and technology for the Union. Close to the policy-making process, it serves the common interest of the Member States, while being independent of special interests, whether private or national.

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